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RAYS OF POSITIVE ELECTRICITY

AND THEIR APPLICATION TO CHEMICAL ANALYSES

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RAYS OF POSITIVE ELECTRICITY

AND THEIR APPLICATION TO

CHEMICAL ANALYSES

MONOGRAPHS ON PHYSICS.

EDITED BY

SIR J. J. THOMSON, O.M., F.R.S.,

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RAYS OF POSITIVE ELECTRICITY

AND THEIR APPLICATION TO CHEMICAL ANALYSES

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WITH ILLUSTRATIONS

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PREFACE.

I HAVE endeavoured in this book to give some account of the experiments on Positive Rays which have been made at the Cavendish Laboratory during the last seven years, and which have been the subject of papers scattered through the Philosophical Magazine, the Proceedings of the Royal Society, and the Proceedings of the Cambridge Philosophical Society. I have, in addition, included a short account of the researches of Stark and others on the Döppler effect in Positive Rays and of Gehrcke and Reichenheim's experiments on Anode Rays, as these, those on the Döppler effect especially, are very closely connected with the results obtained by the very different methods described in the earlier part of this book. I have described at some length the application of Positive Rays to chemical analysis; one of the main reasons for writing this book was the hope that it might induce others, and especially chemists, to try this method of analysis. I feel sure that there are many problems in Chemistry which could be solved with far greater ease by this than by any other method. The method is surprisingly sensitive—more so even than that of Spectrum Analysis, requires an infinitesimal amount of material, and does not require

3146

this to be specially purified: the technique is not difficult if appliances for producing high vacua are available. I am glad to be able to take this opportunity of expressing my obligations to Mr. F. W. Aston, B.A., and Mr. E. Everett. My thanks also are due to the President and Council of the Royal Society for permission to use the blocks illustrating my Bakerian Lecture.

J. J. THOMSON.

CAMBRIDGE, 4 *October*, 1913.

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RAYS OF POSITIVE ELECTRICITY.

THE positive rays were discovered by Goldstein in 1886.[1] His apparatus is represented in Fig. 1; the cathode K which stretched right across the tube *r* was a metal plate through which a number of holes were drilled, the diameter of the holes being considerably less than the thickness of the plate; the axes of the holes were at right angles to the surface of the plate; the anode *a* was at the end of the lower part of the tube. The pressure of the gas in the tube was so low that when the electrodes K and *a* were connected with the terminals of an induction coil and a discharge passed through the tube, the dark space below the cathode was well developed. Under these circumstances Goldstein found that slightly diverging bundles of a luminous discharge streamed through the holes in the cathode into the upper tube. The colour of the light in these bundles depended on the kind of gas with which the tube was filled: when it was air the light was yellowish, when it was hydrogen, rose colour. These rays can be shown very conveniently by the use of the tube represented in Fig. 2; a form also used by Goldstein in his earlier experiments. The cathode which fills the middle of the tube is a flat disc with a hole in it; a metal tube fitting into the hole is soldered

[1] Über eine noch nicht untersuchte Strahlungsform an der Kathode inducirter Entladungen. "Berl. Ber.," XXXIX, p. 691, 1886; "Wied. Ann.," LXIV, p. 38, 1898.

on to the cathode, the length of the tube should be several times the diameter of the hole and its axis perpendicular to the plane of the cathode; the anode is a wire fused into the upper part of the tube. When the pressure of the gas is properly adjusted, the positive rays stream through the tube into

FIG. 1.

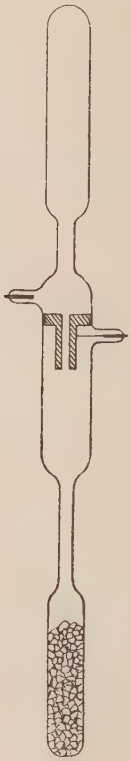


FIG. 2.

the lower part of the vessel while the cathode rays shoot upwards. The contrast between the colour of light due to the positive rays and that due to the cathode rays is, when some gases are in the tube, exceedingly striking. Of all the gases I have tried for this purpose neon gives the most striking

results, for with this gas the light due to the positive rays is a most gorgeous red, while that due to the cathode rays is pale blue; with helium the positive rays give a reddish light while that due to the cathode rays is green. The spectroscopic examination of the light due to the positive and cathode rays reveals interesting differences which we shall have to consider later; we may anticipate, however, so far as to say that the character of the light produced by the positive rays is similar to that of the velvety glow which, in an ordinary discharge tube with an unperforated cathode, spreads over the surface of the cathode.

As in Goldstein's experiments these rays were observed streaming through holes or channels in the cathode; he called them "Kanalstrahlen". Now that they have been proved to be streams of particles, the majority of which are positively electrified, it seems advisable to call them positive rays, as indicating their nature; the name Kanalstrahlen only suggests the methods of demonstrating them.

Many important properties of the positive rays can be easily demonstrated by the use of a tube like that shown in Fig. 2. For example when the rays strike against the glass sides of the tube they make the glass phosphoresce. The phosphorescence produced by the positive rays is of a different colour from that produced by the cathode rays and is in general not nearly so bright. With German glass the positive and cathode rays both produce a greenish phosphorescence, though the greens are of different shades. With some substances the contrast is much more striking, for example with fused lithium chloride the phosphorescence produced by the positive rays is an intense red showing when examined by the spectroscope the red lithium line; the phosphorescence due to the cathode rays is a light blue giving a continuous spectrum. The phosphorescence due to the positive rays is a most

valuable aid for studying the way the rays are deflected by electric and magnetic forces, and it is important to find the substance which gives the brightest phosphorescence. The substance which I have found most useful is willemite, a natural silicate of zinc. The mineral should be ground into as fine a powder as possible, the powder shaken up in alcohol so as to form a suspension, which is allowed to deposit slowly on a glass plate; by this means the glass is covered with an exceedingly even deposit of the willemite. After continued exposure to the positive rays the brightness of the phosphorescence diminishes and ultimately disappears, so that for the detection of these rays the willemite must be renewed from time to time. Some substances deteriorate more rapidly than others, for example zinc blende phosphoresces very brightly under the positive rays, but, as far as my experience goes, it deteriorates much more quickly than willemite, so that when the observations have to last for any considerable time the willemite is preferable. A more sensitive, and for many purposes more convenient, way of registering the deflection of the positive rays is to take advantage of the fact that, when these rays strike against a photographic plate, they affect the plate at the place of impact and thus a permanent record of the position of the rays can be obtained. The action of the rays on the plate differs from that of light, since these rays do not use the whole thickness of the film but only a layer close to the surface, so that it does not follow that the most "rapid" photographic plates are the most sensitive to the positive rays. The most sensitive plates for the detection of the positive rays would be those having very thin films containing as much silver as possible. I have tried the old Daguerreotype process instead of the usual dry plate method, but without much success. It is probable that if Schumann plates (Baly's "Spectroscopy," p. 359) could be prepared as uniform and free from streaks as

ordinary commercial plates they would be the most suitable for the study of the positive rays; all the plates of this kind I have tried, however, have been too streaky to permit the determination of faint lines with any certainty. The plates known as "Imperial Sovereign" give very good results.

The positive rays gradually remove a thin deposit of metal from the part of walls of the tube against which they strike. Such thin deposits can readily be produced by running an electric discharge through the tube when it contains gas at a low pressure, using for the cathode a piece of the metal it is wished to deposit on the glass. The metal cathode "splutters" and the metal is deposited as a thin layer on the glass near the cathode.

DOUBLE CATHODES.

Goldstein [1] found that positive rays came freely from the space between two parallel plates metallically connected together and used as a cathode for the discharge through gas at a low pressure. Cathode rays also come from this region, and the discharge from a cathode of this kind, through a gas where there is a marked difference in colour between the luminosity produced by the cathode and positive rays, presents some very interesting features. Hydrogen, and to a still greater degree helium and neon, are suitable gases for this purpose. When a cathode formed of two parallel equilateral triangles connected together by a wire is used for the discharge through helium at a low pressure, the discharge near the cathode has the appearance represented in Fig. 3. From the points of the triangle stream pencils of luminosity showing the characteristic red colour of the positive rays in helium, while the middle points of the sides

[1] Goldstein, "Phil. Mag." VI, p. 372, 1908.

are the origin of streams of greenish luminosity, the colour of the path of the cathode rays through helium. The difference in the character of the rays is also made evident by bringing a small magnet near the discharge tube; the green rays are visibly deflected by the magnet but no appreciable effect is produced on the red rays. By using polygons instead of triangles, or scalene triangles instead of equilateral ones, very interesting distributions of the red and green pencils can be

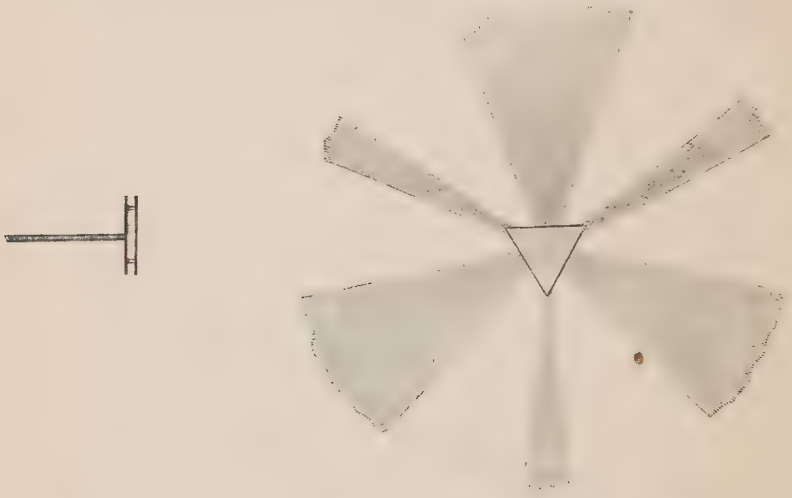


FIG. 3.

obtained. Researches on these parallel cathodes have been made by Kunz[1] and Orange,[2] and they are often useful for giving strong pencils of positive rays in definite directions; we shall have to consider later on examples of their use for this purpose.

[1] Kunz, "Phil. Mag.," VI, xvi, p. 161, 1908.
[2] Orange, "Proc. Camb. Phil. Soc.," XV, p. 217.

RECTILINEAR PROPAGATION OF THE POSITIVE RAYS.

This can be shown by placing a solid obstacle in the path of a pencil of positive rays: this casts a shadow on the part of the tube which was phosphorescing under the impact of these rays. Comparing the shape of the shadow with that of the obstacle, it is found that the shadow is very approximately the projection of the outside of the solid on the walls of the tube by lines passing through the hole in the cathode through which the pencil of positive rays emerges.

On the Nature of the Positive Rays, their Deflection by Electric and Magnetic Forces.

As cathode rays were proved to be negatively electrified particles by the study of the deflections they experience when acted on by magnetic and electric forces, and as these deflections gave the means of finding the mass and velocity of the cathode particles, it was natural to attempt to apply the same methods to the positive rays. It was not, however, until twelve years had elapsed since the discovery of the rays that any effect of a magnetic field on them was detected. A small permanent magnet held near a bundle of cathode rays produces a very appreciable effect; it has, however, no apparent action on the positive rays: as a matter of fact the deflection due to a magnetic field on the positive rays is at most about 2 per cent of the deflection of the cathode rays, the deflections being measured at equal distances from the cathode. In 1898, however, Wien, by the use of very powerful magnetic fields, proved that the positive rays were deflected by magnetic forces.[1]

Before discussing Wien's experiments it will be convenient

[1] W. Wien, "Verh. d. phys. Gesell.," 17, 1898.

to consider the theory of the deflection of a moving electrified particle by a magnetic field. The force acting on the moving particle is at right angles to the magnetic force, at right angles also to the direction of motion of the particle and equal to $e\mathrm{H}v\sin\phi$, where H is the magnetic force at the particle, v the velocity of the particle, ϕ the angle between H and v, and e the charge on the particle. Since this force is always at right angles to the direction of motion of the particle it will not alter the speed of the particle but only the direction in which it is moving. Suppose that the particle is originally projected with a velocity v parallel to the axis of x, and that it is moving in a magnetic field arranged so as to be very approximately in the direction of the axis of z, the direction of the force along the particle will be parallel to the axis of y and this will be the direction in which it will be deflected. If y is the deflection in this direction at the time t, m the mass of the particle, H the magnetic force parallel to the axis of Z, and e the charge carried by the particle, the equation of motion of the particle is

$$m\frac{d^2y}{dt^2} = e\mathrm{H}\frac{dx}{dt}.$$

Integrating this equation we get

$$m\frac{dy}{dt} = \int_o^t e\mathrm{H}\frac{dx}{dt}\,dt = \int_o^x e\mathrm{H}dx \qquad (1)$$

if the origin of co-ordinates is taken at the point of projection; for since the particle was projected parallel to the axis of x, $\frac{dy}{dt} = o$ when $x = o$. Now if the deflection of the particle is small $\frac{dx}{dt}$ will, neglecting the squares of small quantities, be equal to v, and $\frac{dy}{dt}$ to $v\frac{dy}{dx}$. On this assumption equation (1) may be written

$$mv\frac{dy}{dx} = \int_o^x e\mathrm{H}\,.\,dx\,;$$

hence if y is the deflection when $x = l$

$$mvy = \int_o^l \left\{ \int_o^x e\mathrm{H}\,dx \right\} dx.$$

integrating by parts we have

$$mvy = l\int_o^l e\mathrm{H}dx - \int_o^l xe\mathrm{H}dx$$

$$= e\int_o^l (l - x)\,\mathrm{H}dx$$

or writing A for

$$\int_o^l (l - x)\,\mathrm{H}dx$$

$$y = \frac{e}{mv}\,\mathrm{A}.$$

Where A depends merely upon the strength of the magnetic field and the distance from the point of projection at which the deflection is measured; it is quite independent of the charge mass, or velocity of the particle.

If the magnetic field is that between two poles of an electromagnet placed close together and reaching up to the point of projection of the particle, then if a is the breadth of the pole pieces, H is approximately constant from $x = o$ to $x = a$ and vanishes from $x = a$ to $x = l$. Substituting this value for H in the expression for A we find

$$\mathrm{A} = a\left(l - \frac{a}{2}\right)\mathrm{H}$$

when H is the magnetic force between the poles. When this approximation is not sufficiently accurate and we have to take into account the stray magnetic field beyond the poles as well as the variation of the magnetic force between the poles, A may be conveniently determined by the following method.[1] Wind a coil of triangular section DEF, the base DF being

[1] J. J. Thomson, "Phil. Mag.," VI, XVIII, p. 844.

equal to l, the angle EDF a right angle, and DE small compared with the depth of the pole pieces of the electromagnet. Place the coil so that DF is along the direction in which the particle is projected. D being at the point of projection and F at the distance at which the deflection is measured, connect up the coil with a ballistic galvanometer, or what is

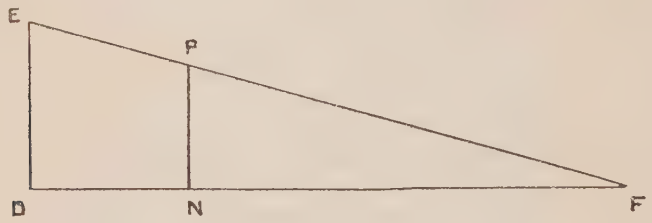


FIG. 4.

more convenient with a Grassot flux meter, and determine the number of lines of magnetic force which pass through this coil when the electromagnet is made or broken ; from this number we can easily determine the value of A. For if N is this number, then we see from Fig. 4 that

$$N = \int_0^l H \times PN \, . \, dx$$

and from the figure

$$\frac{PN}{DE} = \frac{FN}{FD} = \frac{l - x}{l}$$

$$\text{hence } N = \int_0^l H \, . \, \frac{DE}{l} (l - x) \, dx$$

$$= \frac{DE}{l} \int_0^l H(l - x) dx$$

$$= \frac{DE}{l} \, . \, A.$$

Thus when N is known A can be at once determined.

ELECTROSTATIC DEFLECTION OF THE PARTICLE.

Let us suppose as before that the particle is projected with a velocity v parallel to the axis of x: let the electric force acting on the particle be parallel to the axis of z and equal to Z, then the equation of motion of the particle under the electric force is

$$m\frac{d^2z}{dt^2} = eZ$$

When the deflection is small, $\frac{d^2z}{dt^2} = v^2\frac{d^2z}{dx^2}$ approximately, and hence

$$mv^2\frac{d^2z}{dx^2} = eZ$$

$$\text{or} \quad z = \frac{e}{mv^2}\int_o^l\left(\int_o^x Z dx\right)dx$$

$$= \frac{e}{mv^2}\,\mathrm{B}$$

$$\text{where B} = \int_o^l\left(\int_o^x Z dx\right)dx$$

thus B is quite independent of the charge, mass, or velocity of the particle, and depends merely on the distribution of the electric field and the distance from the point of projection at which the deflection is measured.

A very convenient method of producing the electric field is to have two parallel plates perpendicular to the axis of z; in this case the electric field is approximately constant between the plates and vanishes outside them. If b is the length of the plates measured parallel to the axis of x, and if one end of the plates just comes up to the point from which the particle is projected, putting $Z = Z$ from $x = o$ to $x = b$, and $Z = o$ from $x = b$ to $x = l$, we find that $\mathrm{B} = Zb\left(l - \frac{b}{2}\right)$

so that if z is the deflection when $x = l$

$$z = \frac{e}{mv^2} \mathrm{Z}b\left(l - \frac{b}{2}\right).$$

The electric field is not absolutely constant between the plates, it is greater close to the edges than in other parts of the field, nor does it absolutely vanish at all places outside the plates; when great accuracy is required these points have to be taken into account in the calculation of B. A method by which this may be done was given by the author in the "Phil. Mag.," VI, vol. xx, p. 752.

If the particle is simultaneously acted on by magnetic and electric forces parallel to the axis of z, we may, if the deflections are small, superpose the effects due to the magnetic and electric forces, so that the y, z deflections of the particle parallel to the axis of y and z respectively are given by the equation

$$y = \frac{e}{mv} \mathrm{A} \quad (1)$$

$$z = \frac{e}{mv^2} \mathrm{B} \quad (2)$$

Thus if we had a stream of charged particles of different kinds (i.e. with different values of e/m) projected from the origin with different velocities parallel to the axis of x, in the absence of electric and magnetic forces they would all strike a screen at $x = l$ at the same point. When, however, they are submitted to the action of electric and magnetic forces they get sorted out, and no two particles strike the same point on the screen unless they are moving at the same speed and also have the same value of e/m. If we know the deflected position of the particle we can by equations (1) and (2) calculate both the values of v and also the value of e/m; we have from these equations

$$v = \frac{y}{z} \frac{\mathrm{B}}{\mathrm{A}} \quad (3)$$

$$\frac{e}{m} = \frac{y^2}{z} \frac{\mathrm{B}}{\mathrm{A}^2}. \quad (4)$$

Thus y/z will be constant for all particles moving with a given speed whatever may be their charge or mass, hence all such particles will strike the screen in a straight line passing through the undeflected position of the particles.

Again for the same kind of particle y^2/z is constant whatever may be the velocity of the particles, hence particles of the same kind will all strike the screen in a parabola with its vertex at the undeflected position of the particles, and there will be as many of these parabolas as there are different kinds of particles.

Wien's Proof of the Magnetic and Electric Deflection of the Rays.

W. Wien[1] applied this method to demonstrate the magnetic and electric deflections of the positive rays; he proved in this way that the positive rays contained electrified particles, and the direction of the deflections showed that they

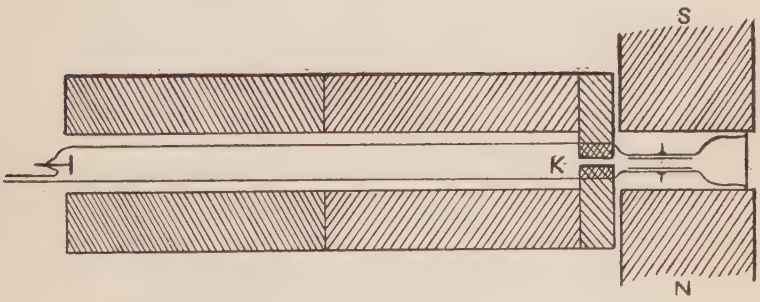


Fig. 5.

were positively charged. He calculated by the formula we have just given the values of e/m and v for these particles.

The method used by Wien is illustrated in Fig. 5.

The cathode K was an iron cylinder 3 cm. long with a

[1] W. Wien, "Wied. Ann.," 65, p. 440, 1898; "Ann. der. Phys.," 8, p. 244, 1902.

hole 2 mm. in diameter bored through it, the anode was at the top of the tube. The lower end of the tube was made as flat as possible so as to facilitate the observation of the spot of luminosity produced by the impact of the positive rays on the glass. The magnetic field was produced by an electromagnet whose poles were at N and S: it is necessary to shield the part of the tube through which the discharge is passing from the magnetic field; if this were not done the discharge would be so much affected by the magnet that trustworthy observations would be impossible; the tube was shielded by surrounding it with thick sheets of soft iron. The electrostatic field was produced between two parallel metal plates which were connected with the terminals of a voltaic battery. When the magnetic and electric fields were acting, the round spot of phosphorescence due to the positive rays coming through the hole in the cathode was drawn out into a straight band. Since the band was straight the velocities of the different particles producing it would all be the same; the values of e/m for these particles would, however, all be different. When the tube was filled with hydrogen, Wien found that the value of e/m for the most deflected portion was 7545, the value of e/m for a charged atom of hydrogen in the electrolysis of water is 10,000. In his first set of experiments Wien found that on filling the tube with oxygen the value of e/m for the most deflectible rays was 9800 in one experiment, in later experiments after very pure oxygen had flowed through the tube for a long time he found on first passing the discharge through the tube very much smaller values of e/m than for hydrogen, but the higher values reappeared after the discharge had passed for a short time.

The deflections of these rays by the electric and magnetic fields show that they are positively charged particles, the values of e/m obtained for these particles show also that

they are very much more massive than the particles in the cathode rays for which $e/m = 1{\cdot}7 \times 10^7$. The displaced particles in this experiment were spread out into a continuous straight band, indicating, according to the theory of the effect of electric and magnetic fields on charged particles, that in the positive rays there are particles giving all values of e/m from zero up to about 10,000. This would imply, assuming that the charge on each particle is the same, that the masses of the particles vary *continuously* from a certain value comparable with the mass of an atom of hydrogen up to a value which is very large in comparison with this mass. This *continuous* variation in the value of e/m is contrary to what might be expected, for, from the molecular theory of gases, the masses available in the gas would not vary continuously but would increase by finite steps, the smallest step being the mass of the atom of hydrogen: again the results of many different lines of investigation lead to the conclusion that e like m does not vary continuously, but that all electrical charges are multiples of a unit charge whose value in electrostatic measure is $4{\cdot}8 \times 10^{-10}$. Again it would appear from the uniformity of the luminosity produced by the displaced positive rays that there is no special kind of atom which is predominant among these rays. For if there had been a great excess of particles of one kind, these would have produced a very bright spot on the glass if they had all been moving with the same velocity, or a bright arc of a parabola if they had been moving with varying velocities. The experiments which I will now describe, which I made in 1906, show that the discrepancies between the theory and the experiments are due to the pressure of the gas in the discharge tube in Wien's experiments having been so high that the particles forming the positive rays collided with the molecules of the gas whilst they were passing through the electric and magnetic fields. The effect of these collisions is to ionize the

gas so that the gas through which the positive rays have to pass is full of charged particles, some charged with positive others with negative electricity. The result of the presence of this electrification is that some of the positive ray particles which were charged before they entered the electric and magnetic fields have their charges neutralized before they pass through them, and thus do not experience the full deflection. On the other hand others which had got neutralized before they entered the field strike against a corpuscle or atom and get ionized by the collision, losing a negative corpuscle. In this way they acquire a positive charge in the field and are

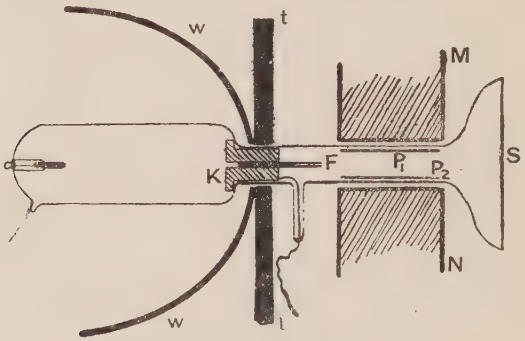


FIG. 6.

deflected by an amount which depends upon the stage in their journey at which they picked up the charge. Thus the quantities we denoted by A and B (see page 12) vary from particle to particle, and the values of e/m cannot be obtained from equations of the type (3) and (4) where A and B are calculated on the supposition that the particles are charged for the whole of the time they are between the poles of the magnet and the plates of the condenser.

In my first experiments [1] on this subject the arrangement was as follows: The cathode K (Fig. 6) had a hole bored through

[1] J. J. Thomson, "Phil. Mag.," VI, XIII, p. 561.

it and in this hole a tube F with a very fine bore was firmly fixed; it is essential to the success of the experiment that the bore of the tube should be exceedingly fine so as to get a small, well-defined patch when the positive rays strike the screen, S. This was a flat glass plate uniformly covered with powdered willemite which phosphoresces much more brightly than glass when struck by the rays. M and N are the poles of the electromagnet, and P_1 P_2 the parallel metal plates used to produce the magnetic and electric fields respectively; *t*,*t*, W,W are

FIG. 7.

FIG. 8.

sheets of soft iron to screen the discharge taken from the magnetic field due to the electromagnet.

The effect observed on the screen depends to a very great extent upon the pressure of the gas in the tube; when this was not exceedingly low, the phosphorescence under the action of the magnetic and electric fields was drawn out into two continuous straight bands as in Fig. 7. The value of e/m for the most deflected portion of the band *a*, was 10^4, for that of band *b*, 5×10^3. These correspond to the values of e/m for the atom and molecule of hydrogen respectively, suggesting that the one band is due to hydrogen atoms, the other to hydrogen

molecules. When the tube contains helium there are three bands to be seen as in Fig. 8. The values of e/m at the tips of these bands are respectively 10^4, 5×10^3, $2 . 5 \times 10^3$, indicating that we have here again bands due to the atom and molecule of hydrogen, and in addition a new one due to atoms of helium, for (as the atomic weight of helium is 4) e/m for the helium atom is one quarter of that for the hydrogen atom. It is remarkable that the slope of these bands, and therefore, by page 12, the velocity of the particles, varies little if at all with the potential difference between the anode and cathode of the discharge tube. This potential difference may be increased three or four times without producing any appreciable effect upon the slope of the bands of phosphorescence. When air is in the tube, the appearances of the bands is much the same as when the tube contains hydrogen, though the phosphorescence is not so bright. The most conspicuous things on the screen in this case are the two bands corresponding to the atom and molecule of hydrogen respectively.

In addition to the two bands deflected in the direction indicating a positive charge on the particles, there is another fainter band deflected in the opposite direction which must therefore be due to particles with a negative charge. The value of e/m for the tip of this band is 10^4, thus these negative particles are not cathode rays for which e/m is $1 \cdot 7 \times 10^7$, but have a mass equal to that of an atom of hydrogen. The existence of particles deflected in the opposite direction to that of the majority of the particles had also been observed by Wien.

EFFECT AT VERY LOW PRESSURES.

When the pressure is reduced to as low a value as is possible the appearance of the luminosity on the screen

entirely changes. At these low pressures it is exceedingly difficult to get the discharge to pass through tubes of moderate size when the cathodes are made of aluminium or any of the metals ordinarily used for this purpose, and there is great danger of sparks passing through the glass and breaking the tube. This can be avoided to a great extent by facing the cathode with a thin layer of calcium, or smearing the face of the cathode with the liquid alloy of sodium and potassium. This reduces considerably the difficulty of getting the discharge to pass and diminishes the risk of perforating the tube. The appearance at these low pressures when hydrogen or air is in the tube is shown in Fig. 9. It will be noticed that the straight bands of phosphorescence have almost disappeared and that most of phosphorescent light is concentrated into two parabolic curves which are connected with the undeflected spot by straight faintly luminous lines. The value of e/m for one parabola is 10^4, that for the other 5×10^3 so that they are due to the atom and molecule of hydrogen respectively. At these low pressures the luminosity in the negative direction disappears. But both at the low and higher pressure there is, even when the magnetic and electric fields are in action, an appreciable amount of luminosity at the position occupied by the undeflected spot.

FIG. 9.

There is considerable advantage in using very large glass vessels for the discharge tubes when studying positive rays; with large vessels the pressure can be made very small before the tube offers great resistance to the passage of the discharge through it. The increase in the difficulty of getting the discharge to pass comes in at the pressure when the dark space round the cathode reaches the walls of the tube. When

the tube is big the walls are far away from the cathode and the pressure has to be exceedingly low before the dark space reaches the sides of the tube. We can work with much lower pressures with these large tubes and therefore reduce the obstruction which the positive rays meet with in their passage from the cathode to the screen. Using vessels of about 2 litres capacity I have observed[1] on a willemite screen the parabolas corresponding to carbon, oxygen, neon, and mercury vapour as well as those corresponding to the atom and molecule of hydrogen and the atom of helium. The photographic plate is, however, for most purposes a much more

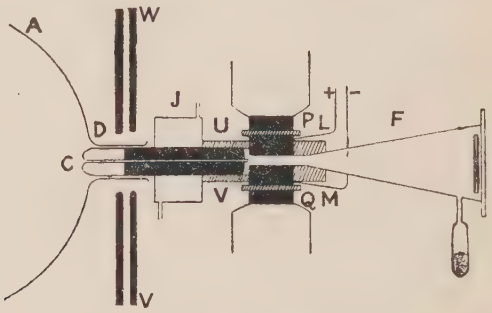


FIG. 10.

convenient detector than a willemite screen. It is more sensitive, it gives a permanent record, and measurements can be made with much greater accuracy on the plate than they can on the screen. Before entering into the discussion of the theory of the positive rays it is desirable to describe the results obtained with the photographic method, as well as the experimental details by which these results have been procured.

The apparatus now in use at the Cavendish Laboratory is represented in Fig. 10. The discharge takes place in a large

[1] J. J. Thomson, "Phil. Mag.," VI, xx, p. 752, 1910.

glass flask A : a volume of from one to two litres is a convenient size for this purpose. The cathode C is placed in the neck of the flask. The position of the front of the cathode has a very considerable influence on the brightness of the positive rays and ought to be carefully attended to. The best position seems to be when the front of the cathode is flush with the prolongation of the wider portion of the flask. The shape of the cathode is represented in section in Fig. 11 : the face of the cathode is made of aluminium, the other portion is soft iron. A hole is bored right through the cathode to admit the fine tube through which the positive rays are to pass. Care should be taken to bore this hole so that its axis is the axis of symmetry of the cathode. The tube through which the positive

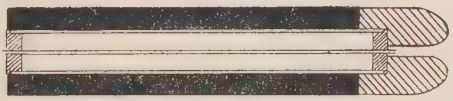


Fig. 11.

rays pass is fastened into the cathode in the way shown in Fig. 11.

The bore of this tube will vary with the object of the experiment. If very accurate measurements are required, the diameter of the tube must be reduced to ·1 mm. or less. With these very fine tubes, however, very long exposures (1½ to 2 hours) are necessary. The length of the tube is about 7 cm. The tubes are prepared by drawing out very fine bore copper tubing until the bore is reduced to the desired size. The tube is straightened by rolling it between two plane surfaces, and great care must be taken to get the tube accurately straight, as the most frequent cause of dimness in the positive rays is the crookedness of the tube. After long use the end of the tube nearest the discharge tube gets pulverized by the impact of the positive rays, and the metallic dust sometimes silts up

the tube and prevents the rays getting through. The cathode is fastened in the glass vessel by a little sealing-wax, and a similar joint unites it to the ebonite box, UV. To keep the joints cool and prevent any vapour coming from the wax, the joints are surrounded by a water jacket J through which a stream of cold water circulates.

The electric field is produced between the faces of L and M which are pieces of soft iron with plane faces. These are fitted into the ebonite box UV so that their faces are parallel: the distance between the faces should be small compared with their lengths. In many of the experiments described subsequently the length of the faces was 3 cm. and their distance apart 1·5 mm. Their faces are connected with the terminals of a battery of small storage cells: in this way any required difference of potential can be maintained between them.

These pieces of soft iron practically form the poles of an electromagnetic, for the poles of the electromagnet P and Q are made of soft iron of the same cross section as L,M; they fit into indentations in the outside of the ebonite box and are only separated from the pieces L,M, by the thin flat pieces of ebonite which form the walls of the box. This arrangement makes the magnetic field as nearly coterminous as possible with the electric, which is desirable in several of the experiments. A conical glass vessel F 40 cm. long is fastened by wax to the ebonite box while the other end is fixed to the apparatus which contains the photographic plate. One form of this, designed by Mr. Aston, is represented in Fig. 12. The photographic plate is suspended by a silk thread wound round a tap T which fits into a ground glass joint; by turning the tap the thread can be rolled or unrolled and the plate lifted up or let down. The plate slides in a vertical box B made of thin metal; this is light tight except at the openings A which are placed so that the positive rays can pass through them. The open-

ings are on both sides of the box and about 5 cm. in diameter. When the silk thread is wound up the strip DEFG of photographic plate in the box is above the opening A, so that there is a free way for the rays to pass through A and fall on a willemite screen behind it. This screen is not used for purposes of measurement, but only to see before taking the photograph that the tube is giving an adequate supply of positive rays. The box is sufficiently large to hold a film long enough for two or more photographs; if it is wished to take two photographs, the plate is lowered until the bottom half comes opposite to the opening A, a photograph is taken in this position, the plate is then let down still further until the top half of the plate comes opposite to the opening, then a second photograph is taken. This plan is convenient because the deflections of the different kinds of positive rays differ so much that it is

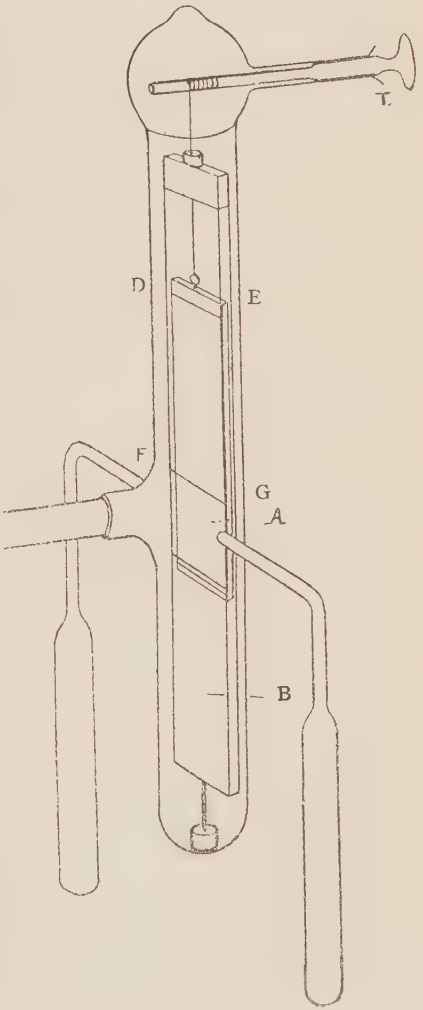


FIG. 12.

difficult to measure them accurately when they are all on one plate. For example the magnetic deflection of the hydrogen atoms is about fourteen times that of the mercury one, thus if the deflection of the hydrogen atom is within the limits of the plate, that of the mercury atom would be too small to measure accurately. When we can take two photographs, however, without opening the tube, we may take one with a small magnetic field to get the deflection of the hydrogen

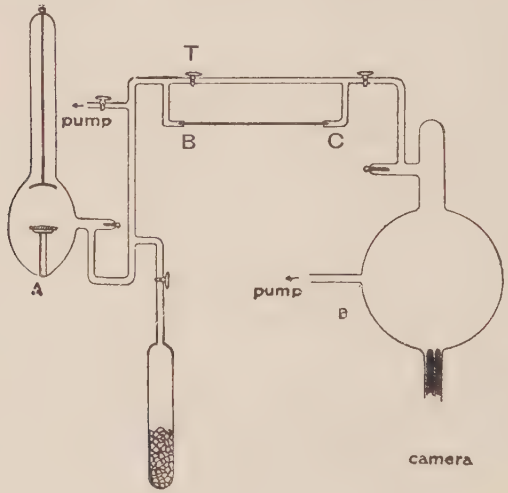


FIG. 13.

atom, and the second with a much larger one to get the deflection of the mercury one.

Two tubes containing coco-nut charcoal are fused to this part of the apparatus; by immersing these in liquid air the pressure can be made exceedingly small. As the only communication between this part of the apparatus and that through which the discharge passes is through the long and very narrow tube in the cathode, it is possible to have the pressure on the camera side of the apparatus very much less than the pressure on the side through which the discharge is passing.

A Gaede pump worked by a motor is connected with the discharge tube, and keeps the pressure in this part of the apparatus at a suitable value. When the rays in some particular gas are under examination a constant stream of this gas is kept flowing through the discharge tube. The gas is stored in the vessel A, Fig. 13, over a column of mercury: this vessel is connected with the discharge tube by the system shown in Fig. 13, where BC is an exceedingly fine capillary tube. When the tap T is turned the gas has to pass through this capillary: it does so exceedingly slowly. The rate can be

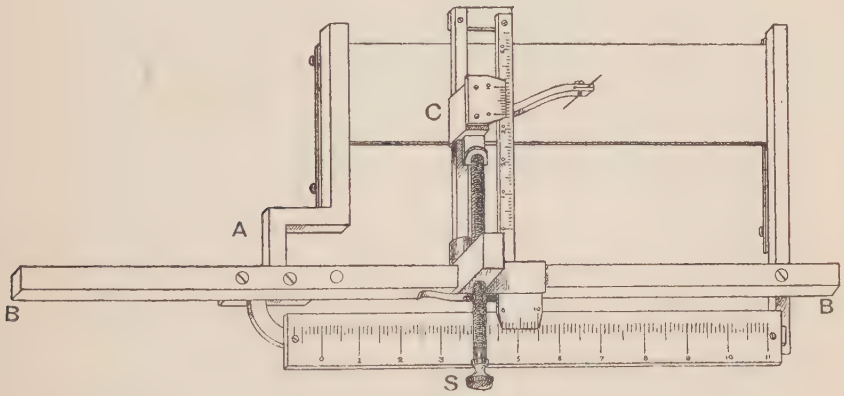


Fig. 14.

adjusted by raising or lowering a mercury reservoir connected with A, this is held in such a position that when the Gaede pump is in action the pressure in the discharge tube is such as to give well developed positive rays. To screen off the magnetic field due to the electromagnet, thick iron plates V,W, Fig. 10, are placed round the neck of the tube.

The curves on the photographic plates made by the positive particles are measured by the apparatus represented in Fig. 14. The photographic plate is clamped in a holder A, and the position of any point on it is determined by moving

the carrier C until the tip of the needle NN comes just over the point in question. The carrier C has two movements, one parallel to the base BB, and the other, by means of the screw S, at right angles to this direction, the position of the point is read off on the two verniers. The plate is placed in the holder so that the direction of the magnetic deflection is parallel and that of the electrostatic deflection, at right angles, to BB.

DISCUSSION OF THE PHOTOGRAPHS.

The appearance of a typical photograph produced by the impact of the cathode rays on the plate when the pressure on the camera side of the apparatus is reduced to about ·001 mm. of mercury is shown in Fig. 15, Plate I. In this and the following figures the deflection due to the magnetic field is vertical, while that due to the electrostatic field is horizontal. It will be seen that the curves on the plate are of two different types.

1. A series of separate parabolic arcs, often of considerable length. From the theory given on page 13 it will be seen that each of these parabolas arises from particles having the same value of e/m, and that these particles have retained this charge throughout the whole of the journey through the electric and magnetic fields. As the velocity of a particle is by equation (3), p. 12 proportional to the tangent of the angle which the line joining the origin to the point where the particle hits the screen makes with the horizontal, it follows that there is a considerable range of velocities among the particles having the same value of e/m. In many cases we have velocities among the same kind of particles differing as much as to make the velocity of the slowest ones less than one fifth that of the fastest. In some cases the parabolas are of fairly uniform intensity along the whole of their length. In others as in that

PLATE I.

FIG. 15.

FIG. 16.

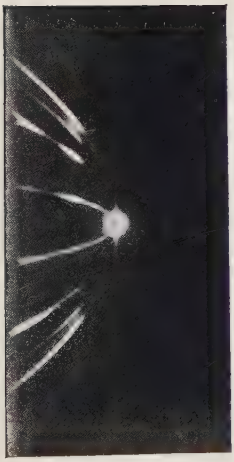


FIG. 17.

FIG. 19.

shown in Fig. 16, Plate I., the head of the parabola (the part least deflected) is considerably brighter than the rest of the curve, while sometimes, as in the case represented in Fig. 17, Plate I., there are several spots of maximum luminosity dotted along the parabolic arc.

With some exceptions (to be considered later) the heads of all the parabolas are in the same vertical line, showing that the minimum electrostatic deflection suffered by the particles which produce these curves is the same for all the different kinds of particles. By equation (2) page 12 the electrostatic deflection is proportional to e/mv^2. If the energy of the particles is due to the fall of the charge through a potential difference V

$$\tfrac{1}{2}mv^2 = \mathrm{V} \cdot e$$

so that $\frac{e}{mv^2} = 1/2\mathrm{V}$. Hence as the minimum electrostatic deflection is the same for all the particles, we conclude that the maximum potential through which the various particles have fallen is the same for all particles. It is natural to conclude that this maximum potential is the difference of potential between the anode and cathode of the discharge tube. It is easy to verify that when the pressure is altered so as to increase this difference of potential the deflection of the heads of the parabolas diminishes.

2. Besides the parabolas there are on the plate a series of straight lines connecting the parabolas with the origin. These are due, I think, to particles which have been charged during a part only of their passage through the electric and magnetic fields. This might happen in two ways. A particle which had got neutralized before reaching these fields might, while passing through them, come into collison with a corpuscle, get ionized, and acquire a positive charge, and during the rest of its journey be deflected by the electric and magnetic forces. Or again a particle might be positively charged when it

entered the fields, attract a corpuscle whilst in them, get neutralized, and for the rest of its journey be free from electric and magnetic deflections. This view of the origin of these lines seems to me to be proved by the following experiments.

As on this view these lines are due to particles which are charged or discharged in the electric and magnetic fields; their intensity, as compared with that of the parabolas, ought to diminish if the length of these fields is reduced. To test this I took a photograph with a tube when the lengths of the electric and magnetic fields were reduced to 1 mm., the intensity of the fields being increased in proportion so as to get deflections comparable with those in the longer fields. With this very short field the straight lines disappeared, and nothing except the parabolas and the undeflected central spot was to be seen on the photographic plate.

Another way of testing this view is to use magnetic and electric fields, which are not coterminous. Let us suppose for example that the magnetic field stretches beyond the electric, on the camera side. There will be a part of the field where the particles are exposed to magnetic but not to electric forces. If a neutralized particle gets ionized in this region, it will experience magnetic, i.e. vertical deflection but no electrostatic or horizontal deflection. Thus with a field of this kind we should expect the line due to particles which acquired their charge whilst in the electric field to have the shape shown in Fig. 18. The straight vertical stem near the origin is due to the particles ionized beyond the electric field, a piece running up to join the parabola to those ionized inside this field, the portion close to the parabola being due to particles which get ionized almost as soon as they enter the fields. Photographs taken with the magnetic field overlapping the electrostatic show this effect very plainly; one of them is reproduced in Fig. 19, Plate I., another in Fig. 25, Plate II.

Let us now consider the case of the charged particles which get neutralized while passing through the field. The part of the line near the origin will be due to particles which get neutralised almost as soon as they enter the field. We have supposed that the magnet was moved towards the camera so that its field overlapped the electric on that side. This will tend to make the electric field overlap the magnetic on the other side, i.e. the side nearest the cathode, so that when a particle first enters the field its deflection is mainly due to the electrostatic force and is therefore horizontal; thus a particle which gets neutralized at the early stages of its journey through the

Fig. 18.

Fig. 20.

fields will have a horizontal displacement abnormally large compared with the vertical; so that the curves produced on the photographic plate by the particles which get neutralized will have a shape something like that shown in Fig. 20. We see that with these overlapping fields we can distinguish between the lines which are due to particles which have gained a charge in their journey and those which have lost one. The concavities of the two curves are in opposite directions. These two sets of lines are very prominent in photographs taken with apparatus in which care has not been taken to make the fields coterminous; an example of this is shown in Fig. 19, Plate I.

If the fields are coterminous and uniform the two curves coincide and are straight lines passing through the origin.

The gain or loss of the charge on the particles in the positive rays is shown very directly by the following experiments:[1] The positive rays were produced in a tube made so as to allow room for two electromagnets A and B, Fig. 21, to be inserted between the cathode C and the willemite screen S. The magnets were placed so that the magnetic field due to the one nearest the cathode was horizontal and the deflection due to it therefore vertical, while the field due to the magnet next the screen was vertical and the deflection due to it horizontal.

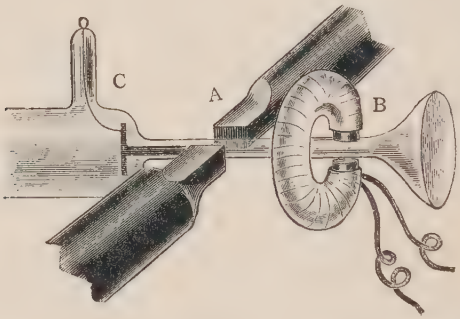


FIG. 21.

The deflections due to the two magnets could thus be separated and measured independently. The effects observed when the magnets were applied separately and then in succession are interesting. A typical case is represented in Fig. 22.

Fig. 22 (*a*) represents the appearance of the screen when the electromagnet next the cathode is the only one in action: *a* is the position of the undeflected spot, *b* that of the deflected. *a* and *b* are connected together by a straight band of luminosity; the luminous streak above *a* is due to negatively charged particles. Fig. 22 (*b*) represents the appearance when

[1] J. J. Thomson, "Phil. Mag.," VI, XVIII, p. 824, 1910.

both magnets are on. If there had been no loss or gain of charge the only effect of the second field would be to remove the spot b horizontally to another place b', and we should have only two spots visible a and b'. We see that as a matter of fact there are four spots a, a', b, b' on the screen, as well as considerable luminosity over the rectangle with these points as corners. Let us consider these spots in succession: b' has experienced the full horizontal as well as the full vertical deflection: it is

FIG. 22.

therefore produced by particles which have retained their charge whilst passing through both magnetic fields. Let us now take b: this spot has the maximum vertical deflection but no horizontal deflection. Thus the particles producing this spot must have been charged all the time they were in the field of the electromagnet A, but have lost their charge before reaching the field of the electromagnet B. This is an example of a particle losing a charge on its way down the tube. Now consider the spot a': this has not been deflected vertically at all,

therefore it must be due to particles which were uncharged when they were passing the first magnet A. On the other hand it has experienced the full horizontal deflection, showing that the particle must have acquired a charge before reaching the second magnet B. This is an example of particle acquiring a charge during its path. The appearance of the luminosity due to the negatively charged particles shows that these, too, gain and lose negative charges in their passage down the tube.

When we reduce the pressure to the lowest value we can reach by the use of charcoal and liquid air, then with the magnet A on alone we have the spots a and b, Fig. 22. There is no luminosity between them and no luminosity above a, while, when both magnets are on, we have merely the spots a and b'; b and a' have disappeared along with the luminosity inside the rectangle.

We shall call the lines we have just been considering secondary lines, the parabolic arcs primary lines.

It is important to point out that the collision which ionizes a neutral particle and gives it a positive charge must be a collision with a corpuscle and not with a molecule of the gas through which the positive rays are passing; for the mass of a molecule of the gas is comparable with that of the positive ray particle, hence a collision between the two would result in the particle losing an appreciable fraction of its energy and being deflected through a considerable angle. The appearance and inclination of the secondary lines show that the particles suffer little diminution in velocity in these encounters and no appreciable change in direction, hence we conclude that the system with which the particle collides must have a much smaller mass than the particle, i.e. it must be a corpuscle and not a molecule.

The secondary curves finally join the parabolic arcs pro-

duced by the particles which have been charged during the whole of their journey. If the junction occurs at a considerable distance from the head of the primary, care has to be taken in some cases to avoid confusing the secondaries with primaries corresponding to a different value of e/m. Thus, for example, if the shape of the secondary and primary were

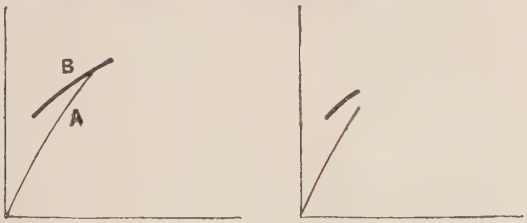


FIG. 23.

similar to that shown in Fig. 23*a*, and the point of junction came off the plate, the appearance on the plate would be that represented in Fig. 23*b*, and the secondary might be mistaken for a primary with a value of e/m less than the true value. If the magnetic field overlapped the electric field on the camera

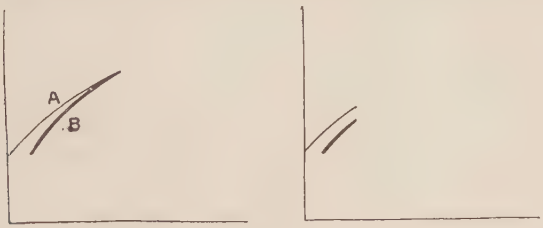


FIG. 24.

side of the apparatus, the primary and secondary would resemble Fig. 23*a*, and if the right hand part were off the plate, the curves would look like Fig. 24*b* and the secondary might be mistaken for a primary with a value of e/m greater than the true value. This possible confusion of a secondary with a primary line is a point which requires careful attention when

the curves produced by the positive rays are used to identify the gases in the discharge tube; for this purpose the primary curves are the only ones that can be relied upon. The tests for a primary line are (1) that it is parabolic, (2) that it shows an abrupt increase in intensity at a point in the same vertical line as the heads of the other parabolas. The first condition is theoretically sufficient, but when only short arcs are available, it is often difficult, unless a very high degree of accuracy is obtained in the measurement of these lines, to tell whether the curve is or is not a parabola.

A very interesting feature about these secondary lines is that the velocity of the particles which produce them is practically independent of the strength of the electric field in the discharge tube. When, as a result of a change in pressure, the potential difference between the anode and cathode increases, the velocity of the particles which produce the primary curves increases also. The speed of the particles which give rise to the secondary curves on the other hand is little if at all affected. A little consideration will show, however, that this is what we might expect from the theory given on page 28. The secondaries are supposed to be due to particles which have gained or lost a charge whilst passing through the electric and magnetic fields. Let us consider firstly the case of the particles which have gained a charge: they must have done so by coming into collision when moving at a high speed with a corpuscle which, as it is in the space behind the cathode where there is no electric field, will be approximately at rest. The effects of the collision will, however, clearly depend only on the *relative* motion of the particle and corpuscle, and will be the same as if the particle were at rest and the corpuscle moving with the velocity of the particle. Now in order that a moving corpuscle may ionize an atom or molecule against which it strikes, the velocity of the corpuscle must exceed a certain value which

recent researches [1] show depends to some extent on the nature of the atom or molecule. Let us call this limiting velocity for a particular kind of atom V; then in order that an uncharged atom of this kind should be ionized when it strikes a corpuscle at rest it must move with a velocity greater than V; hence all the secondary rays of this kind formed by these atoms must have a velocity greater than V. There is thus an inferior limit to the velocity of the secondary rays and this limit depends on the kind of atom which produces these rays. There must, however, be a superior limit to this velocity as well as an inferior one, for these rays are due to particles which move with great velocity and yet can have lost their charge. To have acquired this velocity they must have been positively charged before passing through the cathode or they would not have been acted upon by the electric forces in the discharge tube: and as they are uncharged when they reach the magnetic field they must have got neutralized by combining with a negative corpuscle in the interval. Now a positively electrified particle moving rapidly past a corpuscle could not attract and hold fast the corpuscle if the relative velocity of the particle and corpuscle exceeded a certain value. This velocity is evidently determined by the condition that it is the velocity with which a corpuscle must be moving when it has just sufficient energy to escape from the surface of a positively electrified particle at rest. We should expect the work required to separate a corpuscle from the surface of a positively electrified particle to be of the same order as that required to ionize the particle when neutral, and this work is equal to the kinetic energy of a particle moving with a velocity V. Thus if the velocity of the particle were appreciably greater than V a positively charged particle would not get neutralized, while if the velocity of the neutral particle were appreciably less than

[1] Franck and Hertz, "Verhand. d. D. Phys. Ges.," 15, 34, 1913.

V it would not get ionized. Hence the velocity of the secondaries we are considering must be very approximately equal to V, a velocity which depends only on the nature of the particle and not on the potential difference applied to the discharged tube. This accounts for the fact that the velocities of the particles forming the secondary rays are independent of the potential difference between the anode and cathode.

We can by the method described on page 12 measure the velocity of the particles in the secondary rays corresponding to any atom and hence determine V, the smallest velocity which a corpuscle can have if it is to be able to ionize the atom. When this method is applied to the secondary rays connected with the hydrogen atom we find that V is about 2×10^8 cm./sec. This velocity would be acquired by a corpuscle if it fell through a potential difference of 11 volts. Hence we may take 11 volts as the measure of the energy required to ionize an atom of hydrogen.

To give to the atom of hydrogen this velocity requires a potential difference of $11 \times 1{\cdot}78 \times 10^7/10^4$ volts (taking e/m for the corpuscle to be $1{\cdot}78 \times 10^7$ and for the atom 10^4), this is about 20,000 volts. If it required the same energy to ionize an atom of oxygen as one of hydrogen, V would be the same for oxygen as for hydrogen. To give an atom of oxygen this velocity would require a potential difference of $16 \times 20{,}000$, or 320,000 volts, a much greater potential difference than we usually apply to the discharge tubes. Thus we see that we cannot expect any except the lighter gases such as hydrogen or helium to show secondaries of the type we are considering.

There is, however, another type of secondary—that due to particles which enter the magnetic field in a charged state and lose their charge before emerging from it: this type of secondary, since it arises from the combination of a positively charged particle with a negatively charged corpuscle, might be expected

to occur with slowly moving particles more readily than with fast ones ; a particle moving faster than a certain speed would not combine with a negative corpuscle, so that there would be a superior limit to the speed of the particles in secondary rays of this kind. There does not, however, seem to be any reason why there should be an inferior limit to the velocity, provided the slow particles have managed to retain their charges up to the beginning of the magnetic field, and as a matter of fact this type of secondary often shows itself, as in Fig. 25, Plate II., as the limit of a patch of fogging on the photographic plate rather than as a sharply defined line. There are, however, cases notable with the mercury lines, when this type of secondary is more sharply defined than we should expect, since there are among the particles which produce the primary parabolas some with a smaller velocity than can be detected in the secondaries of this type.

The question arises whether the corpuscles which produce the secondaries by neutralizing a positively charged particle or ionizing a neutral one are free, or are those bound up in the molecules of the gas through which the positive rays are travelling. There are several reasons for thinking that the latter hypothesis is the more probable one.

For if the corpuscles which neutralize the positive particles are free they should be removed by a strong electric field which ought therefore to diminish the brightness of the secondaries. I have, however, never been able to detect an effect of this kind.

Again if free corpuscles were those which neutralized the positively charged particles, the distance such a particle would travel before it got neutralized would depend only upon the density of the free corpuscles. Now this density depends upon the amount of ionization produced by the positive rays after they have passed through the cathode; this will vary

with the number of these rays as well as with the pressure and nature of the gas through which they travel. Consequently the distance a positive particle has to travel before it gets neutralized will depend upon other things besides the pressure and character of the gas, and will not therefore have a very close connexion with the free path of a molecule of this gas. Wien[1] who has made a very complete study of the distance a charged particle travels before it gets neutralized finds that it is of the same order of magnitude as this free path and does not depend upon the number of free corpuscles. This is in favour of the view that the corpuscles which neutralize the positive particles are not free, the process of neutralization seems to be that the positive particles move through the molecules of the gas and pluck out of them the corpuscles required for neutralization.

Again, we conclude for similar reasons that the corpuscles which ionize a neutral particle are not free but bound up in the molecules of the gas through which the positive rays pass. These rays, like the α particles, seem to be able to pass right through molecules, and Königsberger and Kutschewski[2] have shown that when moving through a gas they suffer little diminution in velocity until they are nearly at the end of their path. If the corpuscles which neutralize the positive particles are not free but are in the molecules of the gas through which these particles are passing, we can understand why there is a lower as well as an upper limit to the velocity of the particles which give rise to the secondaries due to particles which have been neutralized while passing through the electric and magnetic fields. For on this view the particle before it can be neutralized has to detach a corpuscle from an atom or

[1] W. Wien, Berlin, "Sitzungsberichte," July, 1911.

[2] Königsberger and Kutschewski, Heidelberg, "Sitzungsberichte," Jan., 1912; "Ann. der Phys.," 38, p. 161.

molecule. To do this requires the expenditure of a definite amount of work which has to be done on the corpuscle by the particle. The energy communicated to the corpuscle depends on the velocity of the particle, and unless this velocity reaches a definite value the corpuscle will not get enough energy to escape from the molecule and will thus be unable to neutralize the particle.

NEGATIVELY CHARGED PARTICLES.

We have already seen (p. 18) that besides the particles which carry a positive charge of electricity there are others which carry a negative one. These negatively charged particles show many analogies with the particles which produce the secondary rays we have been considering. Like them they are particles which have changed their condition after passing through the cathode. Before passing through the cathode they were positively charged and they owe the high velocity they possess to the action on this charge of the electric field in front of the cathode. After passing through the cathode they get neutralized and then attract to themselves a negatively electrified corpuscle which gives them a negative charge. The attraction which brings the corpuscle and the particle together is the attraction between a *neutral* particle and a corpuscle. We may imagine that this attraction is the result of electrostatic induction between the charge on the corpuscle and the particle. The magnitude of this attraction will depend upon how nearly the particle behaves like a conductor of electricity, or perhaps more accurately like a body of very great specific inductive capacity. The greater the specific inductive capacity the greater the attraction, while if the specific inductive capacity is the same as that of the surrounding medium there will be no attraction at all. It is not surprising therefore to find

that different kinds of atoms and molecules differ very greatly in their power of acquiring a negative charge. With two or three exceptions to be mentioned later I have never found *molecules* with a negative charge, though molecules with positive charges are quite common. The exceptions are the molecules of oxygen, carbon, and, though very rarely, hydrogen, and the hydroxyl radicle. It will be noticed that these are elements or radicles, and I have not met with any case when the molecule of a compound has been found with a negative charge, though they are found readily enough with positive charges. I do not mean by this that it is impossible to give a negative charge to a molecule of a compound gas when it is electrically neutral, but merely that the attraction between such a molecule and a negatively electrified corpuscle is so feeble that it is not sufficient to enable the molecule to keep a permanent hold on the corpuscle when it sweeps past it with the velocity with which these molecules move in experiments with the positive rays.

There are some atoms also which I have never observed with a negative charge even when large quantities of them with positive charges were coming through the hole in the cathode. The atoms of helium, nitrogen, neon, argon, krypton, xenon, and mercury belong to this type. On the other hand negatively charged atoms of hydrogen, carbon, and oxygen are found in almost every tube where the pressure is not too low, the negatively charged oxygen atom being specially prominent. If chlorine or any of its gaseous compounds are present in the tube, negatively charged chlorine atoms are conspicuous. The brightness of the lines due to the negatively charged particles, as compared with that of those due to the positive ones, increase rapidly as the pressure increases. At fairly high pressures I have seen the lines due to negatively charged hydrogen

atoms quite comparable in intensity with those due to the positive ones.

Though in one sense all the lines due to negatively charged particles are secondaries they show differences amongst themselves corresponding to the difference between the primary and secondary positive lines. Some of the negative lines like the positive secondaries come close up to the origin, while there are others which, like the primary positives, are finite arcs of parabolas, terminating abruptly when they approach within a certain distance of the vertical axis. Indeed the lines on the negative side are frequently exact reproductions in shape and size of the corresponding lines on the positive. An example of this is shown in Fig. 26, Plate II., where the curves α and β are the lines corresponding respectively to the positively and negatively electrified atoms of oxygen when the discharge passed through very pure oxygen: it will be seen that every detail in the positive curve is reproduced in the negative. This might suggest that the positive and negative atoms were the two halves of a neutral molecule which divided after passing through the cathode. Further consideration, however, shows that this view is not tenable, at any rate in the great majority of cases. The heads of the negative parabolas, like those of the positive, are all on a vertical line and the distance of this line from the vertical line through the origin is about the same as the corresponding distance for the positive parabolas. From this it follows by equation (2) (p. 12) that the maximum value of $\frac{1}{2}mv^2/e$ is the same for the negative as for the positive particles and equal to the potential difference between the anode and cathode of the discharge tube. To take a definite case, let us suppose that the negatively charged hydrogen atom owes its charge to having been in chemical combination with an atom of carbon before it passed through the cathode, the molecule of the compound being positively charged when in the discharge

tube and acquiring then a high velocity under the electric field. After passing through the cathode the molecule gets neutralized and then dissociates into a positively charged carbon atom and a negatively charged hydrogen one. The kinetic energy acquired by the molecule CH, if it had one charge of electricity, would be measured by V, the potential difference between the anode and cathode in the discharge tube. Since the mass of the carbon atom is twelve times that of the hydrogen one, the kinetic energy of the hydrogen atom would correspond to a fall of potential V/13, so that if this atom went through the same electric and magnetic fields as the positively charged carbon atom, the horizontal deflection of the hydrogen atom would be twelve times that of the carbon one. The photographs show, however, that the deflections are equal. Again if the negatively electrified oxygen atoms had previously been in combination with an atom of hydrogen we should expect that the addition of hydrogen to pure oxygen would increase the brilliancy of the lines due to negatively electrified oxygen. I have never been able to detect any effect of this kind. It is true that when some compounds of oxygen are in the tube the negative lines are brighter than with other compounds. I am inclined to think that the exceptional brightness of the lines is due to the presence of the hydroxyl radicle and that these exceptionally bright lines are OH and not O. The view which seems to accord best with the observations is that given on page 40, that the negatively electrified atoms are atoms which were positively electrified when in the discharge tube, that they got neutralized after passing through the cathode by combining with a corpuscle, and in this neutral condition exerted so strong an attraction upon a corpuscle that they were able to capture it though moving past it with an exceedingly high velocity.

Taking this view, we can form an estimate of the magnitude of the attraction between a neutral atom and a corpuscle.

From the measurement of the plates we find that there are negatively electrified atoms of hydrogen with a velocity as large as 2×10^8 cm/sec. This means that a neutral atom of hydrogen is able to capture a corpuscle even though it is moving past it with this velocity. This capture, however, would not take place unless the work required to remove a corpuscle from the surface of a neutral atom of hydrogen were greater than the kinetic energy of a corpuscle moving with the velocity of 2×10^8 cm./sec. This kinetic energy is equivalent to the fall of the atomic charge through 11 volts; hence we see that it must require an ionizing potential of more than 11 volts to liberate the corpuscle from a negatively electrified atom of hydrogen. The same considerations show that to liberate the corpuscle from a negatively electrified atom of carbon would require at least ·9 volts, while for oxygen the corresponding ratio would be ·7 volts. It must be remembered that these are merely inferior limits: the actual values may be much larger.

As we stated before, it is only some neutral atoms which are able to capture corpuscles when moving with the speed of the positive rays and only very few molecules are able to do so. The nature of the attraction between a neutral atom and an electric charge must, if we regard the atom as made up of corpuscles and positive charges, depend on the freedom with which the corpuscles can move under the field exerted by the charge: if they can move readily the force may be considerable. If on the other hand they are rigidly connected with the atom the force will be very small. A very simple experiment will illustrate this point. Suppose we have a considerable number of small compass needles with agate caps placed on a disk which is suspended from a long string. If we mount the compass needles on needle points fixed to the disk, so that they can turn freely, and then hold a magnet near the disk, the disk

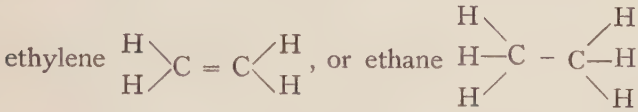
will be strongly attracted towards the magnet. If we take the compass needles off the needle points and lay them on the disk, the friction will prevent their rotation relative to the disk. If we now put the magnet in the same position as it was before it will be found that the attraction has been very much diminished.

Thus we should expect the attraction between a neutral atom and a corpuscle to be very much increased by the presence in the atom of corpuscles which can move freely relatively to the atom. If these freely moving corpuscles are those which are near the surface and which give rise to the forces which bind the atoms in the molecule together, we can readily understand why a neutral molecule should not attract a corpuscle as vigorously as a neutral atom. For when two atoms in a molecule are held together by the forces which they exert on each, the corpuscles in each atom will take up definite positions in their atoms, and will resist any displacement. Their mobility will thus be diminished and they will therefore not exert much attraction on a charge of electricity outside them. We infer that those atoms which like helium do not occur among the positive rays with a negative charge have very few free corpuscles. It is remarkable that so far as we know the atoms of the monatomic gases never occur with a negative charge in these experiments; this is consistent with the preceding theory, for the attraction between two atoms depends on the presence of these mobile corpuscles, and if these are few or sluggish the force may be insufficient to keep two atoms together. It would, as we have seen, require a strong attraction between an atom and a corpuscle to enable the atom to capture the corpuscle in experiments like these we are considering, when the atom moves past the corpuscle with a very great velocity. Franck [1] has shown that even when this

[1] Franck, "Verhand. d. D. Phys. Ges." 12, 613, 1910.

velocity is comparatively small the atoms of a monatomic gas like argon cannot capture a negatively electrified corpuscle.

I have found two cases in which the molecule has occurred with a negative charge, the first of these is carbon. When the discharge tube contains such gases as CH_4, CO_2, CO where there are no bonds between two carbon atoms in the molecule, we find negatively charged carbon *atoms* but no negatively charged molecules. When, however, we use compounds such as acetylene H – C≡C – H,



where, according to the usual interpretation of the constitution of these bodies there are bonds between two carbon atoms in the molecule, then we find molecules as well as atoms of carbon with the negative charge. This is a very interesting result as it shows (1) that there are strong forces between two carbon atoms in a molecule of the compound, forces strong enough to keep them united when the compound molecule is split up; (2) that the corpuscles in the constituent atoms of the carbon molecule have considerable mobility, i.e. that the pair of carbon atoms is not saturated in the sense that a pair of atoms of hydrogen or nitrogen are saturated when they form a molecule. These conclusions are in good agreement with chemical theory. With benzene vapour in the discharge tube I have found, in addition to negatively charged atoms or molecules, negatively charged triplets containing three carbon atoms. I have sometimes thought that in this case I could see indications of a line corresponding to four carbon atoms with a negative charge, but the line has always been so exceedingly faint that I cannot be sufficiently certain of the accuracy of the measurement to be quite sure that it was due to C_4.

The other case in which I have observed a negatively

charged molecule is that of oxygen; the negatively charged oxygen *atom* produces what in many cases is the strongest line on the negative side: the negatively charged oxygen molecule is only met with in exceptional cases. The causes which determine its appearance have not yet been made out: it probably depends on the presence in the tube of some special type of carbon compound. It does not seem to occur in very carefully purified oxygen. I have found it most frequently in oxygen containing a little hydrogen.

ATOMS CARRYING TWO OR MORE POSITIVE CHARGES.

Though the heads of most of the parabolic arcs are situated in the same vertical line, in many cases some of the parabolas, especially those corresponding to the atoms of oxygen and carbon, are prolonged towards the vertical axis. The prolongations do not reach right up to this axis but in many cases, as in the line *a* in Fig. 26, Plate II., which is due to the atom of oxygen, stop after going half-way. These prolongations of the parabolas are also parabolic and are continuations of the primary parabola. They are therefore due to particles which, when they are in the deflecting fields, have the same value of e/m as the particles which produce the primary parabolas. The fact that the smallest horizontal deflection of the prolongation is just half that of the corresponding deflection of the primary shows (see p. 12) that the swiftest of the particles in the prolongation has twice the kinetic energy of the swiftest in the primary. Thus these particles when in the electric field in the discharge tube acquire twice the kinetic energy of the normal particle; they must therefore when in the discharge tube have had twice the normal charge. They must, after passing through the cathode and before getting into the deflecting fields, have

PLATE II.

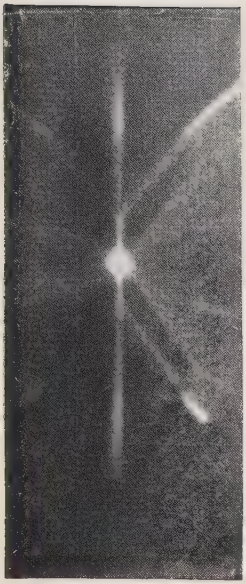


FIG. 25.

FIG. 26.

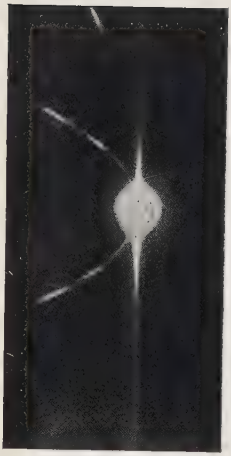


FIG. 27.

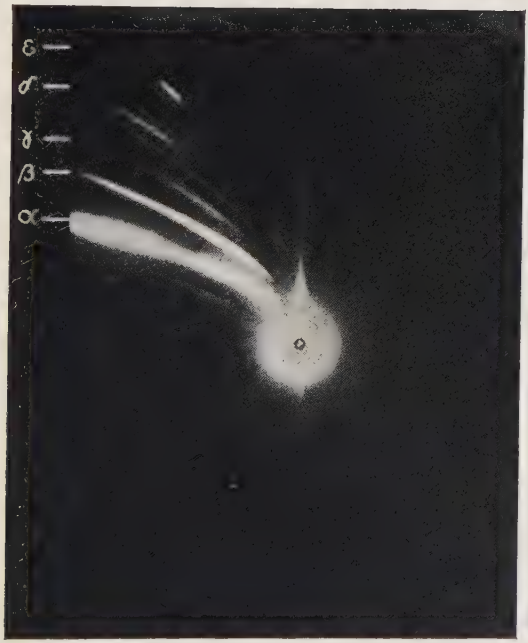


FIG. 28.

had their charge reduced to the normal value. For as we have seen, the value of e/m in these fields is normal, hence if they have retained the double charge they must have double the mass. If, however, they had retained the double charge the electrostatic deflection would have been normal: for though the kinetic energy is doubled, which halves the deflection for normal charge, the charge and therefore the electrostatic deflection for given kinetic energy is doubled too, and hence the result would be the normal deflection, while the actual deflection is only one-half of this. We conclude, therefore, that the prolongation is due to particles which had a double charge when in the discharge tube, but which have lost one of these charges after passing through the cathode.

It is a strong confirmation of this view that when we find these prolongations we generally find on the same plate lines having a value of e/m twice that of the prolongation and beginning in the normal place; these are due to particles which have retained their double charge after passing through the cathode. And conversely when we find these lines corresponding to the double value of e/m we find a tail or prolongation to the line corresponding to the normal value. This would not necessarily be true at pressures so low that the particles did not make any collisions after passing through the face of the cathode, but I have not been able to reduce the pressure to this point.

The prolongations of the parabolas in some cases extend much more than half-way to the vertical axis; this is especially the case with the parabola produced by the positively charged atom of mercury. Fig. 27, Plate II., shows that even when the electric and magnetic fields are strong enough to produce several millimetres deflection in the heads of the parabolas corresponding to the other elements, the head of the mercury parabola is so little deflected that at first sight it seems to coincide with the

origin. When exceedingly large electric fields are used it can be seen, however, that the head of the mercury parabola is distinctly displaced, and on measuring the amount of the deflection it is found to be one-eighth of the normal displacement of the heads of the parabolas corresponding to the other elements.

This, as we have seen, implies that the particles which produce the head of the parabola corresponding to the atom of mercury must have eight times the maximum amount of energy possessed by the normal atom; if the theory given above is true, this means that some of the mercury atoms had, before passing through the cathode, eight times the normal charge, i.e. had lost eight corpuscles. Eight corpuscles is a very large number for an atom to lose, so that if in this case we can obtain independent evidence of such a loss it will be a strong confirmation of the theory.

A study of plates taken with large electrostatic deflections has revealed the existence of seven parabolas due to mercury, corresponding to the mercury atom with 1, 2, 3, 4, 5, 6, 7 charges respectively. The parabola corresponding to eight charges has not been detected, but as the parabolas in general get fainter for each additional charge, it is probably on the plate although not intense enough to be visible. Fig. 28, Plate II., taken from a photograph when the gas in the tube was the residual gas left after exhaustion by the Gaede pump, shows these lines very well. The measurements of m/e for the parabolas on this plate give the following value (m/e is taken as unity for the atom of hydrogen):—

m/e	
200	200/1
102	200/2
66·3	200/3

m/e	
50·4	200/4
44	this is not a mercury line but is due to CO_2
39·8	200/5
33·7	200/6
28·6	200/7.

It will be noticed that the heads of the parabolas corresponding to 1, 2, 3 . . . charges respectively lie on a straight line passing through the origin. This shows (p. 12) that the particles which produce these heads are all moving with the same velocity, and therefore, since each particle is an atom of mercury, that the kinetic energy of the particles at the heads of the parabolas is constant. This is in agreement with the theory, for the heads of all the parabolas are due to particles which before passing through the cathode had lost eight corpuscles. The particles at the head of the parabola corresponding to one charge ($m/e = 200$) has regained seven of these after passing through the cathode; the one at the head of the parabola corresponding to two charges ($m/e = 100$) has regained six and so on; as the charge on these particles when they were in the discharge tube was eight units in each case, they would naturally acquire the same amount of kinetic energy before passing through the cathode.

The question now arises as to how the mercury atom acquires these very various charges. Can an atom of mercury when ionized lose any number of corpuscles from one to eight, or does it always lose a definite number? Take for example a mercury atom with five positive charges: has it got into this condition by losing five charges when it was ionized, or did it originally lose the maximum number eight and regain three subsequently? The photographs suggest, I think, that the second supposition is the correct one, and that in the discharge tube there are two and only two kinds of ionization. By one

of these kinds the mercury atom loses one corpuscle, by the other eight. The evidence for this is as follows: let us suppose for a moment that atoms with any charges from one to eight were produced by the ionization of the atoms of mercury in the discharge tube, and consider what effect this would have on the parabolas corresponding to the mercury atom with one charge. This would be due to atoms of the following kinds:—

Atoms which had lost

(1) 8 corpuscles in the discharge tube and regained 7 subsequently.
(2) 7 ,, ,, ,, ,, ,, 6 ,,
(3) 6 ,, ,, ,, ,, ,, 5 ,,

and so on: the last member of the series being atoms which had lost one corpuscle on ionization and had not regained it.

The parabola seen on the plate would be due to the superposition of the eight parabolas due to these different types of atoms. The head of each of these parabolas would be separated from the head of any of the others: if d were the horizontal deflection of the one due to the atom which had only lost one corpuscle in the discharge tube, $d/2$, $d/3$, $d/4$, $d/5$, $d/6$, $d/7$, $d/8$ would be the horizontal deflection of the heads of the parabolas due to the atoms which had lost 2, 3, 4, 5, 6, 7, 8 respectively. Thus the resultant parabola would for the part which had a horizontal deflection between $d/8$ and $d/7$ consist only of the parabola due to atoms of class (1); the part when the horizontal deflection was between $d/7$ and $d/6$ would consist of two parabolas due to the atoms of classes (1) and (2); the part with the horizontal deflection between $d/6$ and $d/5$ would be made up of the three parabolas corresponding to the atoms belonging to classes (1), (2), (3), and so on. Thus at the distance $d/7$, $d/6$, $d/5$, $d/4$, $d/3$, $d/2$ and $d/1$ we should expect an abrupt increase in the brightness of the curve, for at each of these places a new parabola is added to the old ones; the intensity of the curve would thus not vary continuously but would have a beaded

appearance. The abrupt increase in intensity at the distance d is very marked in the parabola; it is, however, the only one to be detected. The intensity of this parabola is very great and it might be thought that the charges in the intensity might escape detection owing to the breadth of the curve. We may, however, apply the same reasoning to the parabolas which correspond to mercury atoms with three or four charges which are fine and well defined. The intensity of these curves is, however, perfectly continuous and there are no signs of the abrupt variations which ought to occur if the mercury atoms in the discharge tube had charges intermediate between one and eight. This result suggests that the ionization is mainly at any rate of two types, in the one type an atom of mercury loses a single corpuscle, in the other it loses eight. There would thus seem to be two different agents producing ionization in the discharge tube. This is in accordance with another effect shown by many of the plates; on these plates there are well marked differences between the appearance of the lines due to charged atoms and those due to charged molecules. These differences are of various kinds: for example on the plate reproduced in Fig. 29, Plate III., the line α due to the hydrogen atom is of uniform intensity throughout, while β, the one due to the hydrogen molecule, is very faint at the head but intense elsewhere; in others the line due to the atom is uniform while that due to the molecule has a beaded appearance. An example of this is shown in Fig. 30, Plate III. Perhaps the most important point shown by these plates is that when in a mixture of hydrogen and oxygen there are such differences between the lines due to the atoms and molecules of hydrogen, there are similar differences between the lines due to the atoms and molecules of oxygen. A similar result is obtained when the discharge passes through mixtures of nitrogen and hydrogen. It is interesting to observe that if we have along with these gases monatomic

gases, such as helium or mercury vapour, the lines corresponding to the atoms of these gases show the characteristics of both the atomic and molecular lines of the diatomic gases, suggesting that some of the atoms of the monatomic gas have been ionized by the same process as the atoms of the diatomic gas, and others by the process which produced the charged molecules of this gas. There are in the discharge tube at least two kinds of ionizing agents, and it is not unlikely that they produce different types of ionization. These agents are (1) rapidly moving cathode particles moving away from the cathode, and (2) positively charged atoms and molecules moving towards it; either of these agents can, as is well known, produce ionization by collision. We should expect that the cathode particles, since they penetrate into the atom and come into contact with the corpuscles individually—the collision in favourable cases resulting in the detachment of a corpuscle—would give rise to singly charged systems, and if they struck a molecule might detach a corpuscle from one of the atoms without separating one atom from another, producing in this way a positively charged molecule. The collisions between the positively charged atoms and the atoms and molecules of the gas through which they are passing, might be expected to make the atom or molecule struck move off at a considerable velocity, which at first would not be shared by the corpuscles inside the atom. The tendency of the corpuscles to leave the atom depends only upon the *relative* velocity of the atom and the corpuscles inside it, so that the ionizing effect produced by such a collision is the same as if the atom were at rest, and all the corpuscles moving with the velocity acquired by the atom in the collision. Thus if there were several corpuscles connected with about the same firmness to the atom, the result of the atom acquiring a high velocity in a collision might be the liberation of all the corpuscles and the production of a multiply charged atom. Such

PLATE III.

FIG. 29.

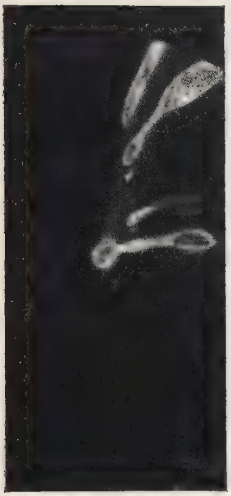


FIG. 30.

FIG. 31.

FIG. 32.

a collision, since it would give one atom in a molecule a great velocity relatively to the other, would tend to dissociate the molecule into atoms and produce positively charged atoms rather than molecules.

The maximum number of charges carried by a multiply charged atom does not seem to be related to any chemical property of the atom such as its valency, but to depend mainly on the atomic weight; thus mercury, the most massive atom on which observations have been made, can have as many as eight charges, crypton atomic weight (82) four or five, argon atomic weight (40) three, neon atomic weight (20) two, nitrogen atomic weight (14), and oxygen (16) two, perhaps in rare cases three, helium also occurs with two charges; the multiple charge has been found on the atoms of all the elements tested with the very suggestive exception of hydrogen: no hydrogen atom with more than one charge has ever been observed, though as the hydrogen lines occur practically on every plate more observations have been made on the hydrogen lines than on those of any other element.

When there are on the plates lines corresponding to atoms of the same element with one, two, three charges, then the larger the number of charges the fainter the line. Judging from the intensity of the lines we should conclude that the number of multiply charged atoms is only a small fraction of the number with one charge. The ratio of the number of atoms which have only one charge to that of those which have two or more charges is very variable and depends on conditions which are not yet fully understood. For example in the case of the carbon atom this ratio seems to depend to a very great extent on the type of gaseous carbon compound in the discharge tube. With some hydrocarbons the doubly charged carbon atoms are relatively much brighter than with others. Again, in the case of oxygen I have found that the purer the

oxygen the fainter was the line due to the doubly charged oxygen atom in comparison with that due to the atom with only one charge. It would thus seem that atoms torn from chemical compounds were more likely to have a double charge than those obtained from a molecule of the element. Chemical combination can not, however, be the only means by which the atoms acquire multiple charges, for the atoms of the inert monatomic gases, neon, argon and crypton, are remarkable for the ease with which they acquire multiple charges.

I have not been able to find any case in which a molecule of either an elementary or compound gas carries a double charge. The line corresponding to the molecule of nitrogen appears on some plates to have a prolongation towards the vertical axis; this would imply a double charge on the nitrogen molecule. I am inclined to think that this prolongation is not really due to the nitrogen molecule, but to the atom of aluminium, as m/e for this atom is 27·5, and for the nitrogen molecule 28, the lines would be so close together that it would be difficult to differentiate them.

Charged atoms on the view we have been discussing are in general produced by the impact of other charged atoms or molecules, while charged molecules are produced by the impact of cathode rays. This must not be taken to imply that cathode rays never produce charged atoms; it is probable that they would do so if they hit one of those corpuscles in the molecule which help, by the forces they exert, to bind the two atoms in the molecule together. There is direct evidence that in some cases charged atoms are produced by cathode rays, for Fulcher ("Astrophysical Journal," 34, p. 388) has shown that the passage of cathode rays through a gas generates in some cases the line spectrum of the gas, and line spectra are regarded as arising from atoms and not from molecules.

But though cathode rays may produce some charged atoms

they more frequently produce charged molecules, the chief source of the charged atoms being positive rays, i.e. rapidly moving charged molecules or atoms. The view that the charged atoms and molecules are produced by different agents helps us to understand the remarkable variations which occur in the relative intensities of the lines due to the atoms and molecules of the same element. To take the case of hydrogen, sometimes the line due to the atom is stronger than that due to the molecule, at others it is weaker. Examples of this are shown in Figs. 31 and 32, Plate III.

Very small variations in the conditions of the discharge are sufficient to produce wide variations in the relative in-

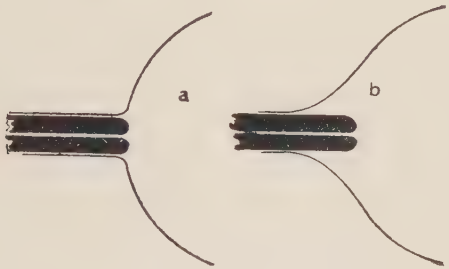


FIG. 33.

tensities of the atomic and molecular lines. If, for example, the cathode is placed so that its face comes inside the neck of the discharge tube as in Fig. 33a, the atomic line of hydrogen is stronger than the molecular: it is weaker, however, when the face protrudes beyond the mouth of the neck as in Fig. 33b. When the cathode is in the position indicated by Fig. 33a the pressure, when the positive rays are at their best, is higher than when the cathode is placed as in Fig. 33b; so that this result suggests that, as the pressure increases, the intensity of the lines due to the atoms as compared with that of those due to the molecules increases also.

METHODS FOR MEASURING THE NUMBER OF THE POSITIVELY ELECTRIFIED PARTICLES.

Though the photographic plate furnishes an excellent means of detecting the existence of positively charged particles of different kinds it is not suitable for comparing the number of these particles present in a bundle of positive rays. For though the intensity of the lines on the photograph will vary with the number of particles, this number will not be the only factor in the expression for the intensity. As an example, consider the lines due (1) to very light particles like the atoms of hydrogen, and (2) to very heavy ones like the atoms of mercury. If these particles have acquired the same amount of energy in the electric field before entering the cathode, the hydrogen atoms will have a velocity about fourteen times that of the mercury ones: they might therefore be expected to penetrate further into the film on the plate and produce a greater photographic effect than the mercury ones. If this expectation is realized, and we shall see that it is, it is evident that the photographic effect cannot be taken as a measure of the number of positively electrified particles.

A method which does give metrical results is founded on the following principle. Suppose that we replace the photographic plate in the preceding method by a metal plate in which there is a movable parabolic slit, then when this slit is moved into such a position that it coincides with one of the parabolas on the photographic plate, positively electrified particles would pass through the slit; if these particles are caught and their total charge measured we shall have a measure of the number of positively electrified particles. Thus if the slit were gradually moved up the plate there would be no charge coming through it, unless it coincided in position with one of the parabolas. As one parabola after another was passed, posi-

tive electricity would come abruptly through the slit, and the amount of the charge would be a measure of the number of particles passing through the slit. If instead of moving the parabolic slit we keep the slit fixed and gradually increase the magnetic field used to deflect the particles, we shall in this way drive one parabola after another on to the slit, beginning with the parabola due to the hydrogen atom and ending with that due to the mercury one, and the charges passing the slits will be proportional to the number of particles.

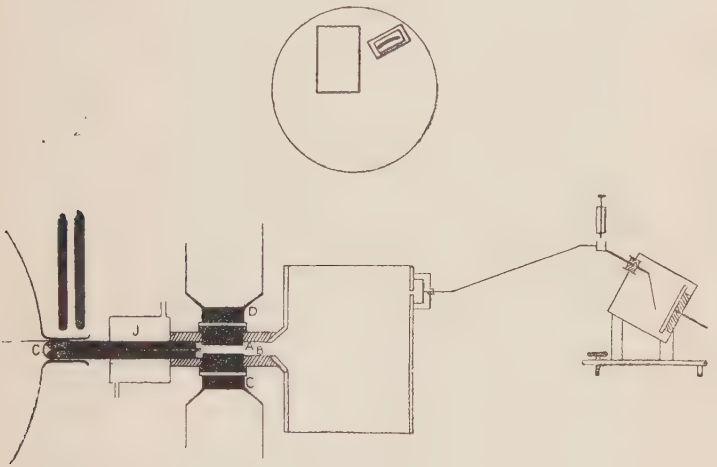


FIG. 34.

The apparatus used to carry this idea into practice is represented in Fig. 34. After passing through the electric and magnetic fields the particles, instead of falling on a photographic plate, fall on the end of a closed cylindrical metal box B. In the end of this box nearest the cathode a parabolic slit about 1 mm. in width is cut, the vertex of the parabola being the point where the undeflected rays would strike the box, and the tangent at the vertex the line along which the particles would be deflected by the magnetic force alone. This slit is the only entry into the box. Inside the box and

immediately behind the slit there is an insulated long, narrow metal vessel placed so that every particle passing through the slit falls into this vessel. This vessel is connected with a Wilson tilted electroscope by which the charge it receives can be measured.

From the front face of the box a portion was cut away, and the opening closed by a willemite screen. The positive rays could be deflected on to this screen and the brightness of the fluorescence observed; in this way one can make sure that the tube is in the proper state for giving positive rays before attempting to make the measurements.

The impact on the face of the box of the rays which do not pass through the slit gives rise to the emission of slowly moving cathode rays; if precautions are not taken these diffuse through the slit, enter the Faraday cylinder, and confuse the measurements. This diffusion can be avoided by placing a small permanent magnet near the slit. The force due to this is strong enough to deflect the more mobile cathode rays without producing any appreciable effect on the positively charged atoms. The pressure of the gas between this box and the cathode should be made as small as possible: the best way of reducing the pressure is to absorb the gas by means of charcoal cooled with liquid air. This method will not produce a good vacuum when the gas in the tube is helium; with hydrogen, too, the vacuum is not so good as for heavier gases, for then the pressure can by this means easily be reduced to 3/1000 of a millimeter.

The method of observing with this apparatus is as follows: The positive rays are deflected by a constant electric field of such a magnitude that the heads of the parabolas are in line with one end of the slit. The magnetic field is then increased by small increments and the deflection of the Wilson electroscope in ten seconds measured. Unless a parabola comes on

the slit there is practically no deflection ; as soon, however, as the magnetic force is such that a parabola comes on the slit, there is a considerable deflection which disappears when the magnetic force is increased so as to drive the parabola past the slit. The appearance and disappearance of the deflection of the electroscope are surprisingly sharp, so that lines quite near each other can be detected and separated. An example of the results obtained by this method is given in Fig. 35. The abscissæ

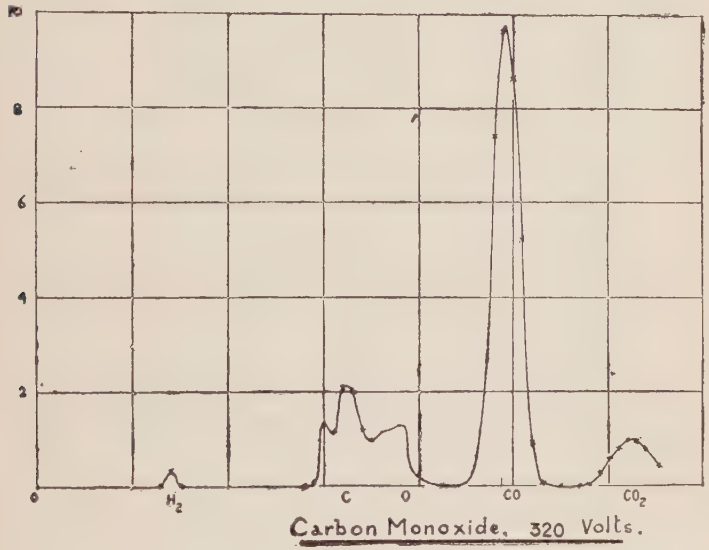


FIG. 35.

are the values of the magnetic force used to deflect the rays, and the ordinates the deflection of the Wilson electroscope in 10 seconds. The gas in the tube was carbon monoxide.

A comparison of this curve with a photograph of the discharge through the same gas shows many interesting features. On the photograph the strongest lines are those corresponding to the atom and molecules of hydrogen. The curve on the other hand shows that the number of hydrogen particles is

only a small fraction of the number of CO particles. The extraordinary sensitiveness of the photographic plate for the hydrogen atom in comparison with that for atoms and molecules of other gases is shown in all the curves taken by this method. But great as is the discrepancy in the case of the photographic plate between the effects produced by hydrogen atoms and an equal number of heavier atoms, it is not nearly so great as it is for a willemite screen : such a screen may show the hydrogen lines very brightly while the CO line is hardly visible, when measurements made with the electroscope in the way just described show that the number of particles of hydrogen is only a few per cent of the number of the CO particles.

It is difficult to get from the photographs any estimate of the relative amount of the different gases in the discharge tube when it contains a mixture of several gases ; for example, if the tube is filled with a mixture of hydrogen and oxygen the relative quantities of these gases may be varied within wide limits without producing any very marked effect on the relative brightness of the hydrogen and oxygen lines in the photograph. This electroscope method is much more metrical as will be seen from Figs. 36 and 37, the first of which represents the curve when the gas in the tube was a mixture of one-third hydrogen and two-thirds oxygen, while in the second, the gas was one-third oxygen and two-thirds hydrogen.

The negatively charged hydrogen atoms seem to have the same preponderance in their effect on the photographic plate over other negative atoms as positive hydrogen atoms have over other positive atoms. Thus on all the plates the line corresponding to the negatively electrified hydrogen atoms is well marked, often being comparable with the negatively electrified oxygen atom. With the electroscopic method the negative hydrogen atom can only just be detected, while the

negatively electrified oxygen atoms produce a large negative deflection. A curve showing the comparative numbers of

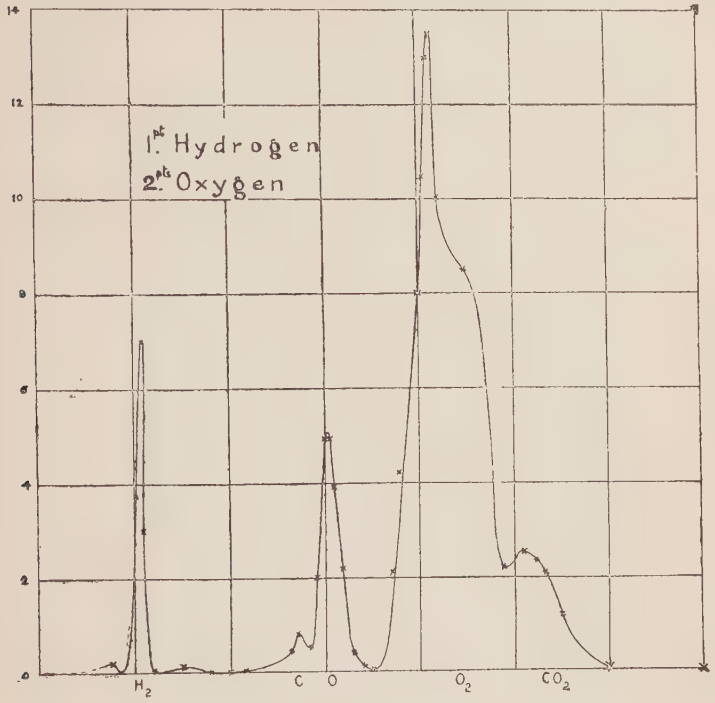


FIG. 36.

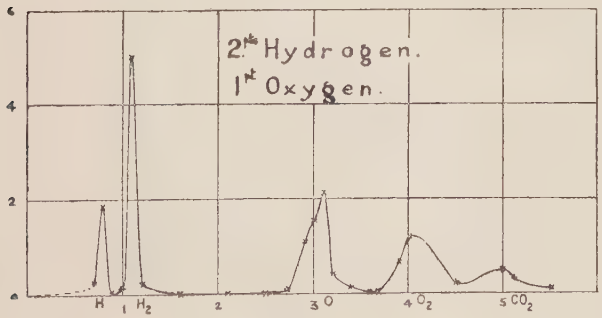


FIG. 37.

different kinds of negatively electrified atoms is shown in the

curve, Fig. 38: the gas in the tube was phosgene, $COCl_2$; the curve at the top of the figure represents the number of negatively electrified particles, the one at the bottom the positively

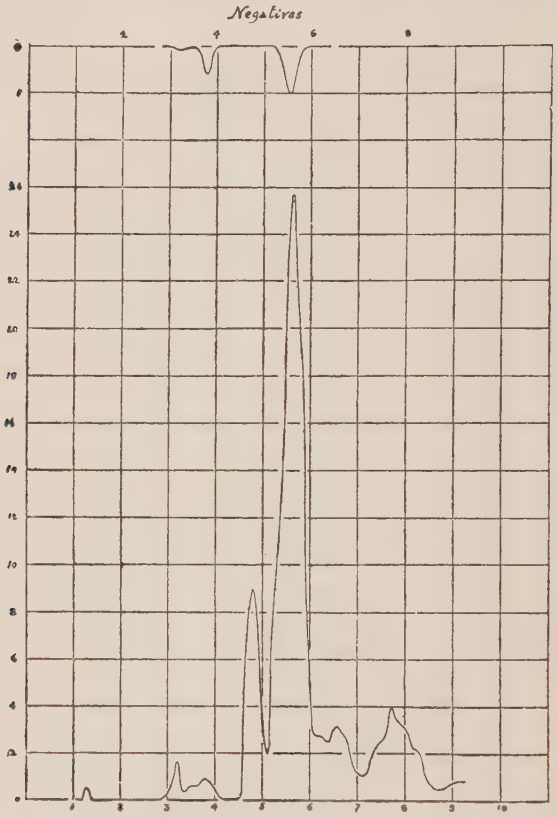


FIG. 38.

electrified ones. It will be seen that the negative atoms detected by the electroscopic method were carbon, oxygen, and chlorine, and that the chlorine atoms were by far the most numerous. On the photographs taken with this gas the line due to

negatively electrified hydrogen seemed comparable in intensity with that due to negative chlorine. An interesting point about the curve representing the distribution of positively electrified atoms is the great variety of atoms and molecules in this case, thus we find atoms of carbon, oxygen, and chlorine, and the molecules CO, Cl_2, CCl, and $COCl_2$. It will be noticed that only a small fraction of the current is carried by free carbon and oxygen atoms, showing that in phosgene the carbon and oxygen atoms are so firmly united that the greater part of them remain together even when the gas is dissociated.

Are the atoms in a molecule of a compound gas charged with electricity of opposite signs?

The study of the curves obtained by the electroscopic method throws some light on the electrical states of the two atoms in a diatomic molecule of an elementary or compound gas. If we regard the forces which keep the atoms together as electrical in their origin, the question naturally arises, are the two atoms in a molecule of hydrogen, for example, charged one with positive the other with negative electricity; or in a molecule of hydrochloric acid gas is the hydrogen atom positively charged, the chlorine negatively, or in a compound like ammonia NH_3 does the nitrogen atom carry three negative charges and each of the hydrogen atoms one positive one?

Let us consider the case of CO for which we have in Fig. 35 the curve which represents the relative numbers of the different kinds of positively charged atoms. If the carbon atom in the molecule were positively, the oxygen atom negatively electrified, then we should expect that if a molecule of CO were split into atoms by the impact of a rapidly moving positively electrified particle, there would be a tendency for the carbon atoms to have a positive charge and for the oxygen ones to have a negative, so that in the positive rays we should expect to find more carbon atoms than oxygen ones. The curve,

Fig. 36, shows that the number of positively electrified carbon atoms exceeds that of the positively charged oxygen ones in the proportion of 11 to 7. These figures, however, underrate the number of oxygen atoms which came through the cathode, for some of them after passing through the cathode acquired a negative charge. The charges given to the electroscope show that the proportion between negatively and positively charged oxygen atoms was as 2 to 7, while the number of carbon atoms which were negatively charged was very small in comparison with that of the positively charged atoms. Taking the negative atoms into account as well as the positive we find that the proportion between the number of carbon and oxygen atoms passing through the cathode is as 11 to 9; the numbers are too nearly equal to allow us to suppose that in the molecule one of the atoms is positively, the other negatively charged.

The curve for $COCl_2$, Fig. 38, shows that the proportion of positively electrified chlorine atoms in the positive rays is not very different from the proportion of chlorine atoms in the normal gas. If the atoms in the molecule $COCl_2$ had individually carried electric charges we should have expected the atoms of the strongly electro-negative element chlorine to have carried a negative charge and to have been relatively deficient in the positive rays.

The view that each of the atoms in a molecule of a compound contains as much positive as negative electricity is supported by considerations drawn from other branches of physics. If the atoms in a molecule of a gas carried separate charges so that one kind of atom was positively, another negatively, charged, then if the gas were dissociated into these atoms the atoms would be charged and the dissociated gas would be a good conductor of electricity. Now there are several gases which are dissociated at low temperatures, nickel carbonyl, for example, is at 100° C. split up into nickel

and CO to a very large extent; if these atoms were charged the electrical conductivity of the gas might be expected to begin to show marked increase at a temperature of about 70° C. when the dissociation first becomes appreciable. The variation of the conductivity of nickel carbonyl with temperature is, however, as Prof. Smith has shown, quite normal, following the same laws as for an undissociated gas. L. Bloch,[1] too, has shown that the dissociation of arseniuretted hydrogen which also takes place at low temperatures is not accompanied by any increase in electrical conductivity. He also showed that many chemical reactions between gases which go on at low temperatures such as the oxidation of nitrogen bioxide, the action of chlorine on arsenic, the oxidation of ether vapour, have little or no effect on the conductivity.

Chemical action, unless accompanied by high temperature, has not been shown to give conductivity. The very vigorous combination of hydrogen and chlorine under sunlight seems to have absolutely no effect on the conductivity of the mixture, and this is a strong reason for supposing that the atoms in the molecule are not charged.

It is true that chemical actions vigorous enough to raise the gases to a very high temperature, such as, for example, the combination of hydrogen and oxygen in the oxy-hydrogen flame, the oxidation in a Bunsen flame, the burning of CO and so on, make the reacting gases good conductors of electricity. This conductivity seems, however, from the result of recent experiments, to be due to the high temperatures produced by the chemical action rather than to that action itself. The conductivity cannot be due to the molecule being dissociated into positively and negatively electrified atoms, for the determinations of the mobility of the negatively electrified particles in flames and gases at a very high temperature show

[1] "Annales de Chimie et de Physique," XXII, pp. 370, 441; XXIII, p. 28.

that it is much larger than would be possible if these particles had masses comparable with that of even the lightest atom. These negatively electrified particles are corpuscles, not atoms, and the electrical conductivity of gases at high temperatures is due to the dissociation of the molecules and atoms into positively charged molecules and atoms and negatively electrified corpuscles, and not to a dissociation such as occurs in solution when the electrified bodies are positively and negatively electrified atoms. The conductivity of hot gases seems to be an example of the emission of corpuscles from hot bodies, rather than to be directly connected with chemical combination. We know that when we raise solids such as metals, or still better, certain oxides to a high temperature they give out copious streams of corpuscles, and the conductivity of flames is better explained by supposing that gases possess this property to some extent than by attributing it to chemical action alone.

We are led by these results to regard the electrical forces which keep the atoms in a molecule together as due not to one atom being charged positively and the other negatively but to the displacement of the positive and negative electricity in each atom. Thus each atom acts like an electrical doublet, and attracts another atom in much the same way that two magnets attract each other.

On the Information Afforded by the Positive Rays as to the Constitution of a Gas, the Nature and Properties of the Molecules, and the Process of Ionization in a Discharge Tube.

The results we have given above enable us to appreciate the importance of the positive rays in investigating the constitution of gases and the properties of atoms and molecules.

In the first place they give a very direct and simple proof of the molecular constitution of gases. We have seen that the

positive rays from a gas produce on the photographic plate a finite number of distinct and sharp parabolas. As each parabola corresponds to a different kind of charged particle this shows that there are only a limited number of different kinds of particles in the discharge tube. The sharpness of the lines shows that all the particles of the same chemical element have to a very high degree of accuracy the same mass. If the atoms of hydrogen, for example, differed appreciably in mass it would not be possible to get on the photographic plates parabolas as sharply defined as those which can be obtained when the tube through the cathode has a very fine bore. As far as we know at present the fineness of the line depends only on the bore of the tube. This would not be the case if there were any variation in the mass of the atoms, for then instead of a line we should get a band bounded on one side by the parabolas corresponding to the heaviest atom and on the other by that corresponding to the lightest.

Again we see that in some gases we have both atoms and molecules, in others only atoms. We can infer from the study of the curves produced by the positive rays that helium, for example, is a monatomic gas, hydrogen and oxygen di-atomic.

The rays show too that the atoms and molecules of the gases can be charged with electricity; all of them, as far as we know, with positive electricity, some of the atoms with negative as well. The circumstances are very unfavourable for a particle in the positive rays to get a negative charge, and we must not conclude that because an atom or molecule has not been observed to acquire a negative charge when in the positive rays it is incapable of doing so under more favourable circumstances.

We have seen too that the atoms of all the elements except hydrogen can acquire more than one unit of positive charge. The maximum number of such units seems to depend on the

atomic weight of the atom, for mercury, the heaviest atom yet investigated, it is as large as eight, for krypton four or five, for oxygen two, and so on. No undoubted case of a double charge on a molecule, whether of an element or a compound, has yet been observed. In addition to the atoms and molecules of recognized elements these rays reveal the existence of radicles and other combinations which are not known to exist permanently in the free state. Thus the positive rays from marsh gas CH_4 show, in addition to the atom and molecule of hydrogen and the atom of carbon, the systems CH_1, CH_2, CH_3, CH_4. The radicle OH with a negative charge has also been found when water vapour was in the tube. We can detect by this method systems which have a very transitory existence, for they need only last long enough to travel from the discharge tube to the photographic plate, a journey which takes less than the millionth of a second.

Again (see p. 45) the rays show that with those compounds of carbon, which contain two or more carbon atoms united by bonds, two carbon atoms connected together are found in the positive rays, and since they are found with a negative as well as with a positive charge, the two carbon atoms united in this way cannot be saturated.

Let us now consider the evidence given by these rays on the question of ionization. We see from the inspection of the photographs that ionization in the discharge tube is not exclusively nor even mainly the detachment of a corpuscle from a neutral molecule: this process would produce merely positively electrified molecules. The photographs show that the products of ionization are much more complex than this: for though we do find the positively electrified molecules of the gas through which the discharge is passing, whether that gas be an elementary one like hydrogen or oxygen or a compound one like carbon monoxide or carbonic acid, these molecules are by no

means the only kind of electrified particles in the rays, indeed they are in general in a minority as compared with electrified atoms. Instead of there being only one kind of carrier for the positive electricity there are always a considerable number of kinds: in an experiment with benzene vapour I counted seventeen distinct kinds of positive carriers. Indeed the splitting up of the gas by the discharge is sometimes so complete that the photographs of the positive rays in different hydrocarbons may be almost identical. Thus, for example, the prominent lines for the vapours of methyl-alcohol, ethyl-alcohol, ether ($(C_2H_5)_2O$) and dimethyl ether are identical, showing that they are due to the products of dissociation of the molecules of these substances and not to the molecules themselves; the lines due to these are very faint.

In the discharge tube then we have dissociation—the splitting up of molecules into atoms—as well as the detachment of a corpuscle from the molecules.

The agents present in the tube which are known by independent experiments to produce ionization are :—

1. Cathode rays of varying velocities moving away from the cathode.

2. Positive rays moving towards the cathode.

3. Rays analogous to Röntgen rays, due to the impact of cathodic and positive rays against the molecules of the gas through which they are passing and also to the recombination of the ions of opposite signs.

The primary effect produced by the impact of a cathode ray with a molecule would be to detach a corpuscle from this molecule. If this corpuscle is one of the structural ones, i.e. one of those causing the attractions which hold the atoms in a molecule together, then the ionization will be accompanied by the separation of the atoms in the molecule: we shall have dissociation as well as ionization and the result will be a

positively electrified atom. If, however, the corpuscle detached is not a structural one the atoms in the molecule will not be separated and a positively electrified molecule will be the result. If this were the only method of ionization we should expect a considerable excess of positively electrified molecules over positively electrified atoms. It is not, however, probable that any large fraction of the ionization in the tube is due to the direct action of the faster cathode rays. The amount of ionization due to such rays has been measured by Glasson[1] who found, as is indicated by theory, that the number of ions produced by cathode ray per unit length of path varies inversely as the kinetic energy of the ray. For rays moving with a velocity of $4{\cdot}7 \times 10^9$ cm./sec. through air at a pressure of 1 mm. of mercury, he found that 1·5 pairs of ions were produced by each ray in travelling over 1 cm. In the experiments with positive rays the velocity of the faster cathode rays was considerably greater than 5×10^9 cm./sec. This would reduce the ionization if the pressure in the gas remained the same, but the pressure in the gas in our experiments was less than ·01 mm. of mercury, so that even if we neglect the diminution in ionization due to increase in velocity, a cathode ray would only produce 1·5 pairs of ions when it had travelled over a metre, a distance much greater than the length of the tube. We conclude that the ionization on the gas is not therefore in the main due to the fast cathode rays: it arises more probably from slow cathode rays and from positive particles. The positive ions from the negative glow when they get into the dark space soon acquire sufficient energy to ionize the gas, producing corpuscles and other positive ions. These secondary corpuscles will at first be moving slowly as they are in a region in the dark space where the electric field is comparatively weak; they will be efficient ionizers as their velocity is small,

[1] "Phil. Mag.," October, 1911.

and will produce other corpuscles by collision, these corpuscles will be in a still weaker electric field and therefore still more efficient ionizers, as it is not until the velocity of the cathode particles sinks below that due to a fall through about 200 volts, that the ionization due to these particles increases as the velocity decreases. Thus near the anode end of the dark space the number of slowly moving cathode rays will increase with very great rapidity, and the gas in this neighbourhood will be a mixture of molecules and comparatively slowly moving cathode rays. Though these rays are slow in comparison with those that have acquired the energy due to the fall in potential through the whole of the dark space, their kinetic energy is large enough to correspond to that due to the thermal agitation of a particle at a very high temperature. For example a corpuscle moving with a velocity 10^7 cm./sec. has energy corresponding to that due to thermal agitation at 0° C.: one moving with a velocity of 10^8 would have energy equal to that due to the thermal agitation at about 27000° C. A velocity of 10^8 cm./sec. would be acquired by a corpuscle through a fall of potential of between 3 and 4 volts, so that the velocity of even the slowest cathode particles in the discharge tube will be considerably greater than this. If there were anything approaching to equi-partition of energy between these corpuscles and the structural corpuscles of the atoms in a molecule, the latter would acquire so much energy that they might wander away from the places they ought to occupy if they are to keep the atoms in the molecule together. The result of this would be that the atoms would separate and some of the corpuscles inside them would have considerable kinetic energy. This energy might be sufficient to carry them outside the atoms and thus produce positively charged atoms: either of the atoms in a diatomic molecule might be positively electrified in this way. The seat of ionization of this kind

would be at the end of the dark space next the negative glow, so that the positively electrified particles produced in this way would fall through the whole of the potential difference in the dark space, and would acquire the maximum amount of kinetic energy, they would therefore hit the photographic plate at the head of the parabola corresponding to this kind of particle. Some of the photographs, such as the one reproduced in Fig. 39, Plate IV., have the heads of the parabolas very much more intense than the rest of the arc, indicating that in this case the majority of the particles have fallen through the maximum potential difference and therefore have been produced at the end of the dark space. There are many cases, however, where this concentration does not occur, and where the arcs of the parabolas are very long, indicating that there is a very considerable range in the kinetic energy of the particles, the uniform intensity of the lines shows that the number of particles is fairly equally distributed over a considerable range of kinetic energy.

We might account for this variation in the kinetic energy in the following ways :—

1. By supposing that the charged particles all started from the same region, the end of the dark space, but before reaching the cathode got neutralized and so were only under the influence of the electric field for a fraction of the journey through the dark space.

2. By supposing that the ionization which produced these particles occurred not merely at the end of the dark space but to some extent throughout the whole of this space.

3. By supposing that the small amount of kinetic energy possessed by some of the particles is due to their colliding with the molecules of the gas whilst passing through the dark space and in this way losing some of their kinetic energy.

Let us begin with the first of these suggestions. We have

seen (p. 32) that unless the pressure is very low some of the particles, after they pass through the cathode, get neutralized and lose their charge for a time; in some cases they acquire it again by being ionized by collision with a corpuscle. If this process went on in front of the cathode as well as behind it we should get variations in the kinetic energy of the particles, as some of them would have passed a larger fraction of their time in the uncharged state than others. The corpuscles which produce neutralization and ionization must be those in the molecules of the gas through which the positive rays are passing and not the free corpuscles. For in the dark space in front of the cathode there is an intense electric field in which the free corpuscles are moving far faster than the particles so that the relative velocity of the particles and free corpuscles is much greater than that of the particles and the corpuscles in the molecules, and therefore the union of the positively electrified particles and the free negatively electrified corpuscles is not likely to occur; there may, however, be some neutralization owing to a positively charged particle uniting with a corpuscle from an uncharged molecule, through which the positive particle is passing.

The third suggestion that the loss of kinetic energy is due to collisions between the particles and the molecules in the discharge tube through which they are moving is open to the objection that it would produce effects of the same general character on all the lines. Thus if all the particles started from the end of the dark space and the reduction in their velocity was due to these collisions we should expect all the lines to show a general resemblance in the way the intensity varied along the parabola. We find, however, on the same plate lines which are quite short, with all the intensity concentrated at the head, and others which are long and of equal intensity throughout. The second suggestion, that positive particles

are produced at different parts of the field by other positively electrified particles in rapid motion, seems to me to indicate an effect which must undoubtedly be largely instrumental in increasing the length of the parabolas. The particles which are produced near the cathode will not, when they reach the cathode, have fallen through as great a potential difference as those produced farther away and will therefore have a smaller velocity.

RETROGRADE AND ANODE RAYS.

The rays we have hitherto been considering consist of positively charged particles travelling in the direction in which such particles would be moved by the electric field in the discharge tube. In addition to these there is another system of rays travelling in the opposite direction. By far the larger portion of these rays are cathode rays, i.e. negatively charged corpuscles moving with great velocity, but as the author showed long ago [1] these are mixed with rays which are evidently of a different character, for unlike the cathode rays they are not appreciably deflected when a permanent magnet is brought near them. It was afterwards shown by Villard [2] and the author [3] that some of these new rays were deflected by strong electric and magnetic fields and that the direction of the deflection indicated that the particles forming the rays were charged with positive electricity. The fact that these rays travel with high velocities away from the cathode and thus in the opposite direction to the electric forces acting upon them makes their investigation a matter of very considerable interest. The apparatus I have used for this purpose is represented in Fig. 40.

A is a perforated electrode through which the rays pass on their way to the willemite screen or photographic plate S. On their journey to S the rays traverse the usual electric and

[1] J. J. Thomson, "Proc. Camb. Phil. Soc.," IX, p. 243.
[2] "Comptes Rendus," CXLIII, p. 673, 1906.
[3] J. J. Thomson, "Phil. Mag.," XIV, p. 359, 1907.

magnetic fields. B is a plane rectangular electrode at the other end of the discharge tube: it is carried by a stopper working in a ground glass joint and thus can be rotated about a vertical axis. C is a wire fused in the side of the tube for use as an auxiliary electrode. D is a side tube in which a closed glass vessel containing a piece of iron can slide up or down: this vessel carries a piece of fine metal rod which, by moving the iron by means of a magnet, can be inserted in or withdrawn from the line of fire of particles projected from B.

When the stopper carrying the electrode B is turned so that the normal of the plane of the electrode either coincides

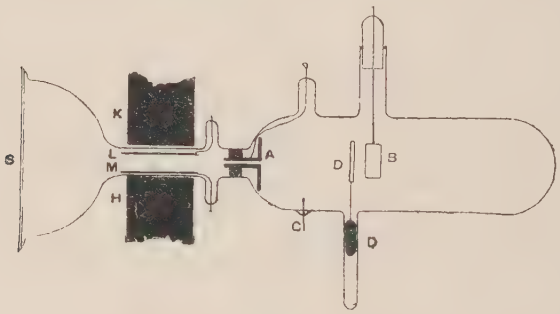


FIG. 40.

with the axis of the hole through A, or makes but a small angle with it, then if B is made cathode and a discharge sent through the tube, the cathode rays pass down through the tube in A and produce vivid phosphorescence on the screen. In addition to these rays there are others which produce a phosphorescence different in colour from that due to the cathode rays and are deflected in the opposite direction by the electric and the magnetic fields: the amount of electrostatic deflection is about the same as that for the cathode rays but the magnetic deflection is very much less. It can easily be shown that these are not ordinary positive rays due to A becoming cathode through accidental reversals of the coil. For

in the first place they disappear when the electrode B is twisted round so that a normal to its plane no longer nearly passes down the tube through A: and secondly the rays persist when A is disconnected from the induction coil and the auxiliary electrode C used as a cathode. Again when the rod attached to D is put in the line of fire a shadow is thrown on the phosphorescence on the screen due to these rays. These rays are strongest when the electrode B is placed so as to be at right angles to the axis of the tube through A. If the electrode is rotated they diminish rapidly in intensity but can be detected until the normal to B make an angle of about 15^0 with the axis of the tube through A; they appear in fact to follow much the same path as the cathode rays from B, for much the same rotation was required to prevent the cathode rays getting through the tube in A and producing phosphorescence on the screen.

These rays get exceedingly feeble when the pressure of the gas in the discharge tube is very low and they are no longer observable at pressures when the ordinary positive rays give quite vigorous effects; even when most fully developed they are feeble in comparison with the ordinary positive rays, so that it is necessary for the tube through A to have a much wider bore than is required for experiments with positive rays. As these rays travel in the opposite direction to the positive rays they are called retro-grade rays.

Using a tube through A about ·5 mm. in diameter I obtained a photograph of the retrograde rays which gave the following results:—

There are in the retrograde rays positively electrified atoms and molecules of hydrogen and positively electrified atoms of oxygen: there are also negatively electrified atoms of hydrogen and oxygen, and with these rays the intensity of the lines corresponding to the negatively electrified particles is greater

than that of the positively electrified ones; with the ordinary positive rays the positive lines are much stronger than the negative. In the retrograde as well as in the positive rays there are large numbers of uncharged particles. The photograph taken with the retrograde rays shows that the maximum velocity of the negatively electrified atom is about the same as that of the corresponding positively electrified one and differs but little from the velocity of these atoms in the ordinary positive rays. This result is suggestive because the electric field in the tube would accelerate the negatively electrified retrograde rays and retard the positively electrified one. It points, I think, to the conclusion that the origin of the retrograde rays is analogous to that of the negatively electrified particles which accompany the positive rays, the difference between them being that the retrograde rays acquire their negative charge before passing through the cathode, while the negative constituent of the positive rays do so after passing through the cathode. We may suppose that the process by which the retrograde rays are produced is somewhat as follows: neutral atoms or molecules acquire a negative charge when they are just in front of the cathode, they are then repelled from the cathode and driven through the dark space, acquiring under the electric field in the discharge tube a velocity of the same order as that acquired by the positively electrified particles of the positive rays during their approach to the cathode. Some of these rapidly moving negatively electrified particles will in their course through the gas come into collision with the corpuscles and molecules in the discharge tubes; the first collision will detach a corpuscle leaving the particle in the neutral condition; another collision will detach another corpuscle and leave the particle positively charged. The particles which have made two collisions form the positively electrified portion of the retrograde rays, those which have made one

collision the portion which is without charge, and those which have not made a collision the negatively electrified portion of these rays.

These retrograde rays are very well developed when a double cathode of the kind introduced by Goldstein (see p. 5) is used instead of a flat cathode. If a cathode consisting of two parallel triangular plates, Fig. 41, is substituted for the flat cathode B in the apparatus, shown in Fig. 40, a plentiful supply of retrograde rays come from the cathode when it is turned into a suitable position. By twisting the triangle round by means of the glass stopper the emission of the rays, both

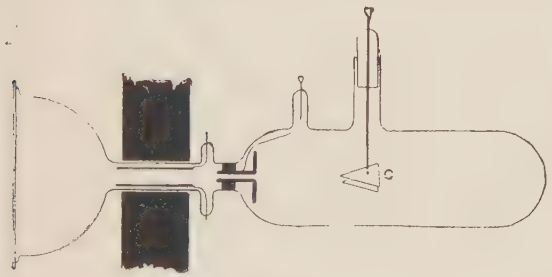


FIG. 41.

cathodic and retrograde, could be determined. In this way it was shown that the maximum emission of cathodic rays is along the line starting from the middle points of the sides. At the higher pressures this is practically the only direction in which cathode rays can be detected; at very low pressures, however, cathode rays can be detected coming from the corners of the triangle as well as from the middle points of the sides. Few, if any, however, are given out in any intermediate direction. The positively electrified particles stream off at all pressures from both the corners and middle points of the sides, but not from the intermediate positions. The most abundant stream comes, as for the cathode rays, from the middle points of

the sides, but the disproportion between the streams from the corners and from the middle points of the sides is nothing like so large as for the cathode rays, so that the ratio of positive to cathode rays is much the greatest at the corners of the triangle.

A simple method of demonstrating the existence of retrograde rays and also of the places at which the positive rays originate is founded on the difference between the phosphorescence of lithium chloride under cathode and positive rays. When lithium chloride is struck by cathode rays, the phosphorescence is a steely blue giving a continuous spectrum. When struck by rapidly moving positively electrified particles the phosphorescence is a rich deep red, and the red lithium line is very bright in the spectrum. To explore the tube for positive rays a thin rectangular strip of mica or metal is covered with fused lithium chloride, the strip is attached to a piece of iron [1] which rests on the bottom of the discharge tube. By moving the iron by means of a magnet the strip can be moved towards the cathode or away from it. If we start with the mica strip close to the cathode we find that there is no red light to be seen on the side of the lithium chloride next the cathode. The anode side of the chloride is a brilliant red, showing that the strip is being struck by the positive rays before they reach the cathode but not by the retrograde ones. If the mica strip is pulled farther away from the cathode until the distance between them is about half the thickness of the dark space, red light appears upon both sides of the strip showing that now it is struck by the retrograde as well as by the positive rays. This state of things continues until the mica reaches the limit of the dark space and approaches the negative glow; in this position the

[1] It is better to put the iron in a closed tube and attach the mica strip to the tube, otherwise so much gas is given out by the iron that it is difficult to reduce the pressure sufficiently.

cathode side of the strip is red but the other side is dark, showing that now it is struck only by the retrograde rays. Another way of making this experiment is to keep the strip fixed at a distance of between one or two centimetres from the cathode. Beginning with a fairly high pressure so that the strip is outside the dark space, we find that the cathode side of the strip is red, while the other side is dark ; in this position the strip is struck only by the retrograde rays. If the pressure is gradually reduced so that the dark space increases until it reaches just past the mica, both sides of the strips will now show the red light, showing that now positive as well as retrograde rays strike the strip. When the pressure is further reduced until the dark space is three or four centimetres long, the red light disappears from the cathode side but is very bright on the other.

These experiments show that many of the positive rays start from close to the junction of the dark space and the negative glow. It is surprising to find how short is the distance which the screen has to travel from the negative glow before the redness of the side remote from the cathode shows that positive rays are striking against it. As at this end of the dark space the electric force is very feeble, the charged particle can only have fallen through a small fraction of the potential difference between the anode and cathode ; yet as we have seen it has the power of exciting the lithium red light. The reason that in the preceding experiment the retrograde rays are not observed when the screen is close to the cathode is due I think to the shadow cast by the mica on the cathode. The mica stops the positive rays on their way to the cathode so that the parts in shadow are not struck by these rays and so cannot be the origin of retrograde rays, if these are produced in the way we have described.

This view is confirmed by the following experiments. If the cathode is placed near the middle of a large bulb and the

mica screen is put a little on one side of the cathode, the red lithium light can be observed on the side of the screen turned towards the cathode even when the screen is quite close to the cathode and the dark space 5 or 6 cm. long.

Again if the cathode stretches across a tube of uniform bore, and the screen is moved towards the cathode, the shadow thrown on the cathode becomes much more marked and suddenly increases in size at the place where the red light fades away from the cathode side of the mica strip. The increase in size is due I think to the screen getting positively electrified when in the region close to the cathode. We know by the distribution of electric force in the dark space that there is a dense accumulation of positive electricity just in front of the cathode, which naturally would charge up an insulator placed within it. The positively electrified screen repels the positively electrified particles which pass it on their way to the cathode and deflects them from their course, so that they strike the cathode beyond the projection on it of the screen. In this way a considerably increased area is screened from the impact of the positively electrified particles. The portion so screened no longer emits cathode rays. Thus the region in front of it is traversed by little if any current and there is consequently no bombardment of the screen by retrograde rays.

Somewhat similar effects are obtained if the mica screen is replaced by a very fine platinum wire. If this wire is slowly moved towards the cathode, starting from a place inside the negative glow, the following effects are observed: almost immediately after entering the dark space the wire becomes red hot and remains so until it reaches the velvety glow immediately in front of the cathode (known as Goldstein's first layer). Here it becomes cold and the shadow which before could hardly be detected now becomes well marked and much thicker than the wire. The change takes place very abruptly. In some

cases just before entering this layer the shadow is reversed, i.e. the projection of the wire on the cathode is now brighter than the rest of the cathode, indicating I think that the wire when in this position gets negatively electrified and attracts the positively electrified particles instead of repelling them.

The retrograde rays are well developed with cathodes made of wire gauze.

ANODE RAYS.

The positively charged particles, which we have hitherto considered, originate in the neighbourhood of the cathode. Gehrcke and Reichenheim [1] have discovered rays of positively charged particles which start from the anode. Their attention was called to these rays by noticing that a pencil of yellow light streamed from a point on the anode of a tube with which they were working. It was found that there had been a speck of sodium chloride at the points on the anode from which the pencil started. They got these rays developed to a much greater extent when they used for the anode a piece of platinum foil with a little pocket in which various salts could be placed. The foil was in circuit with a battery insulated from the one used to send the current through the discharge tube; this battery was for the purpose of raising the anode to a red heat, as these rays are not developed unless this electrode is at a high temperature. The current through the tube was produced by a battery giving a potential difference of about 300 volts which, as a Wehnelt cathode was used, was sufficient to send a very considerable current through the tube: the pressure in the tube was very low. The rays were well developed in this tube when NaCl, LiCl, KCL and the chlorides of Cu, Sr, Ba, In, were placed in the pocket. The colour of the rays corresponded with the colour given to flames by the salt. They did not get any effects when the oxides of calcium or barium were put in the pocket; these oxides are known when hot to give out large

[1] "Verh. D. Phys. Gesell.," 8, p. 559; 9, pp. 76, 200, 376; 10, p. 217.

streams of negatively electrified corpuscles and for this reason are used for Wehnelt cathodes. These rays are apparently only given out by the salts of the metals and not by the metals themselves; they are called Anode rays.

Gehrcke and Reichenheim arranged a Faraday cylinder so that the rays could fall into it; they found that when the rays entered the cylinder it acquired a strong positive charge.

Gehrcke and Reichenheim subsequently used another form

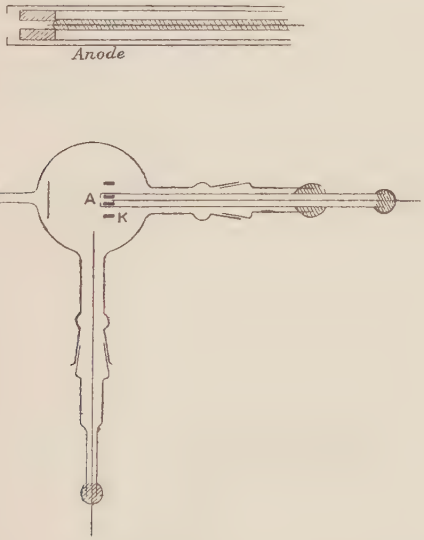


FIG. 42.

of apparatus which gave better results than the one just described. The anode was a rod of salt placed inside a glass tube so that only the front of it was exposed to the tube; the cathode was an aluminium ring encircling the anode, the pressure was reduced to a very small value by the use of carbon cooled by liquid air. With the discharge from a powerful induction coil, or still better from a large electrostatic induction machine, the anode got hot without the aid of an auxiliary heating current, and a bright stream of rays came from the end of the salt anode;

the appearance of this beam is represented in Fig. 43. It was found that a mixture of two or more salts with powdered graphite gave brighter rays than a simple salt, the best mixture seemed to be LiBr, LiI, NaI and graphite. The rays come off

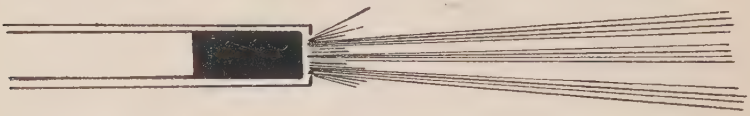


FIG. 43.

at right angles to the surface of the salt; thus if the surface is cut off, as in Fig. 44, the rays come off in the direction *ab*.

Gehrcke and Reichenheim found that there was a very considerable difference of potential between the surface of the anode and a point a centimetre or two away: in some of their experiments it was as much as 2300 volts. By assuming that the energy acquired by the rays was due to the fall through

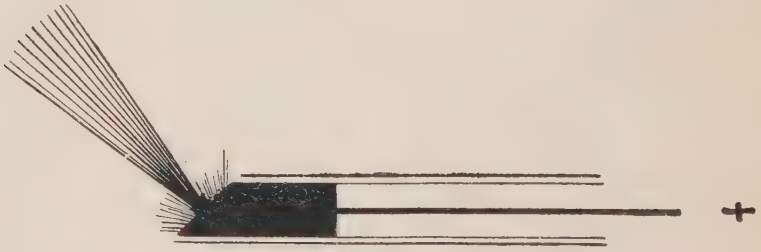


FIG. 44.

this potential V, and measuring the radius of the circle into which the rays were bent by a strong magnetic field H, the values of v and m/e can be determined, for we have

$$\frac{1}{2}mv^2 = Ve$$

and if r is the radius of the circle into which the rays are bent by a magnetic force H at right angles to their path

$$\frac{mv^2}{r} = Hev$$

$$\text{hence} \quad v = \frac{2V}{Hr} \text{ and } e/m = \frac{2V}{H^2r^2}.$$

In this way the following values were obtained :—

Salt.	v. cm/sec	e/m.	ratio of mass of particles to that of an atom of hydrogen.
Li Cl.	$\frac{2\cdot40}{2\cdot71} \times 10^7$	$\frac{1\cdot11}{1\cdot15} \times 10^3$	8·6 – 8·3
Li Cl.	$\frac{1\cdot89}{2\cdot46} \times 10^7$	$\frac{\cdot69}{\cdot87} \times 10^3$	14 – 11
Na Cl.	$\frac{1\cdot87}{1\cdot76} \times 10^7$	$\frac{\cdot46}{\cdot41} \times 10^3$	21 – 23
$Sr Cl_2$.	$1\cdot08 \times 10^7$	$\cdot21 \times 10^3$	90 (if the atom is doubly charged.)

The results for Li Cl given in the first line relate to the brightest part of the rays, those in the second to the least deflected rays. It would appear from this that the charged particles are the atoms of the metal in the salt and that in the case of strontium they carry a double charge. A very interesting case of these anode rays is that of a discharge tube with a constriction in the middle. When two bulbs A and B, about 10 cm. in diameter, with the anode in A and the cathode in B, are connected by a narrow tube: then when the pressure in the tube is very low and a *small quantity of iodine vapour* is introduced into it, anode rays start from the constriction *c* at the cathode end of the narrow tube and cathode rays from *d*, the anode end of this tube. If the connecting tube were quite straight these anode rays might be the positive rays corresponding to the cathode *c*, but as they appear when the tube is bent this cannot be their origin. It is especially to be noticed that the anode rays do not appear unless iodine, bromine, or chlorine is in the tube. This is perhaps due to the fact that the atoms of these substances are excellent traps for negatively electrified corpuscles as they hold these corpuscles imprisoned. Any positively electrified particles in the tube will thus have a much better chance to escape being

neutralized by these corpuscles when these gases are present than when they are absent: and thus the number of anode rays will be increased.

The most natural explanation of these rays is that the hot salts from which they originate act like fused electrolytes, and that the current through them into the discharge tube is carried by the ions into which the salts dissociate, the positive ion, which is a charged atom of the metallic constituent of the salt, following the current will come to the surface of the anode, will get detached from it, and under the influence of the strong electric field which exists in the gas close to the anode will acquire the high velocity characteristic of the anode rays.

DÖPPLER EFFECT SHOWN BY THE POSITIVE RAYS.

Before the methods described in the earlier part of this book had been fully developed, Stark [1] had discovered a property of the positive rays which is of great importance in connexion with the origin of spectra, and incidentally has led to results which have confirmed some of those obtained by the newer methods.

Stark's discovery resulted from the spectroscopic examination of the light produced by the positive rays passing through a gas at a pressure comparable with ·1 mm. of mercury, a very much higher pressure than that used in the majority of the experiments with the photographic plate and the willemite screen. The stream of rays passing through a perforated cathode produces at such pressures in the gas behind the cathode considerable luminosity. Stark examined this luminosity when the gas was hydrogen with a spectroscope: (1) when the line of sight was at right angles to the direction of the rays. (2) When the line of sight was approximately in the direction of the rays. In the first case he found that the series lines for hydrogen were in their normal positions. In the second, however, he found that though there were lines in the normal positions, these lines were broadened out towards the violet end of the spectrum when the positive particles were approaching the

[1] Stark, "Physik. Zeitschr.," 6, p. 892, 1905. "Ann. d. Phys.," XXI, p. 451, 1906.

spectroscope and towards the red end when they were receding away from it, indicating that some though not all of the systems emitting these lines were moving in the direction of the rays with velocities sufficient to give an appreciable Döppler effect. A closer examination of these lines brought out some interesting details which are illustrated in Fig. 45, Plate IV., taken from a photograph by Stark of the hydrogen line $H\gamma$. It will be noticed that though the displaced line is broadened out into a band, this band does not begin at the undisplaced position of the line, but is separated from it by a finite distance. The alteration $\Delta\lambda$ in the wave length λ of a line given out by a source moving towards the observer with a velocity v is by Döppler's principle given by the equation

$$\frac{\Delta\lambda}{\lambda} = \frac{v}{c}$$

where c is the velocity of light. In the case of these small displacements we may take, where we are dealing with one line in the spectrum, $\Delta\lambda$ as proportional to the displacement of the line, and we may also use this equation to determine v the velocity of the particle emitting the line. The fact that the fine line is displaced into a broad band shows that these velocities range over somewhat widely separated limits: this is quite in accordance with the results indicated by the photographs of the positive rays when deflected by electric and magnetic forces. We saw that the parabolic arcs were of considerable length, and therefore were produced by particles moving with a wide range of velocities. The dark space between the undisplaced line and the band indicates that the moving particles do not give out the lines unless the velocity exceeds a certain value. According to Stark and Steubing[1] this limiting velocity varies with the different lines of the same element, increasing as the wave length diminishes. The

[1] "Ann. der. Phys.," 28, p. 974.

PLATE IV.

FIG. 39.

FIG. 45.

FIG. 47.

FIG. 48.

limiting velocity given by these observers for the hydrogen lines are as follows:—

$$H\alpha = 1{\cdot}07 \times 10^7 \text{cm./sec.} \quad H\beta = 1{\cdot}26 \times 10^7 \text{ cm./sec.}$$

These values are approximately proportional to the square root of the frequency of the lines. There is some difference of opinion as to whether this limiting velocity does or does not depend upon the frequency of the light. Paschen[1] came to the conclusion that it was the same for all the hydrogen lines. This velocity is small compared with the average velocity of the positive rays of hydrogen; it corresponds to a fall through a potential difference of less than 100 volts. It is comparable in value with that which the mercury atom acquired in many of the experiments represented by the preceding photographs, when it had possessed one but only one charge throughout its journey through the discharge tube. The maximum displacement of the line depends to some extent on the potential difference between the terminals of the discharge tube; but it does not increase nearly so quickly as the square root of that potential difference, as we should expect if even the most rapidly moving particles could give out the line: the relation between the displacement and the potential difference is given in the following table due to Stark and Steubing.[2] In this table r is the ratio of the kinetic energy of a particle moving with a velocity v calculated by the Döppler formula (p. 90) to the kinetic energy the particle would possess if it fell when carrying one charge through the potential difference between the terminals of the discharge tube.

Potential Difference in Volts.	r.
390	·907
425	·563

[1] "Ann. der Phys.," 27, p. 599.

[2] *Ibid.*, 28, p. 974.

Potential Difference in Volts.	r.
555	·824
600	·716
1200	·622
3000	·358
4000	·309
4000	·402
7000	·274

Stark indeed suggests that his observations are compatible with the view that the deflections approach a limit corresponding to a velocity about $1{\cdot}5 \times 10^8$ cm./sec. and do not exceed this however large the potential difference between the terminals in

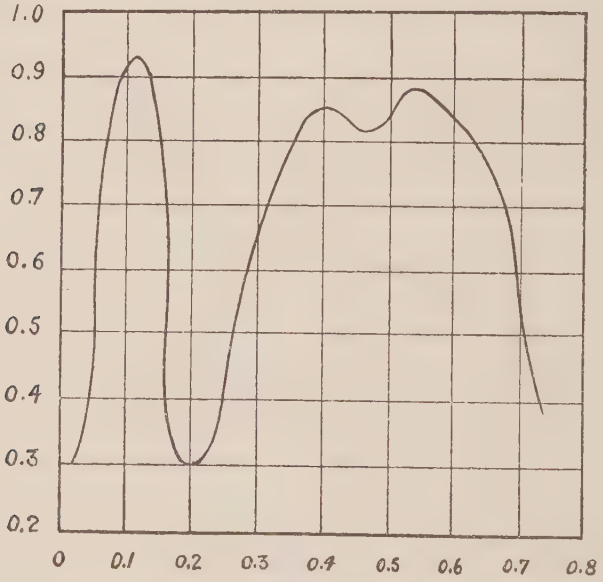


FIG. 46.

the discharge tube may be. The distribution of intensity in the displaced line is very complicated and seems to be affected by the purity of the gas as well as by the potential difference

between the terminals in the discharge tube. Paschen[1] was the first to observe that there are in some cases two maxima of intensity in the displaced line, and this has been confirmed by the experiments of Stark and Steubing[2] and of Strasser.[3] The distribution of energy determined by Hartmann's microphotometer of the $H\gamma$ line in very pure hydrogen is shown in Fig. 46, taken from Strasser's paper. The first peak represents the intensity of the undeflected line, the other two the intensities of the deflected. Gehrcke and Reichenheim[4] have suggested that the atom and the molecule of hydrogen give out the same line spectrum and that the most deflected maximum is due to the atoms, the other to the molecules. If the atom and the molecule acquired the same kinetic energy by falling through the potential difference between the terminals of the discharge tube, the velocity of the atom would be $\sqrt{2}$ times that of the molecule and Gehrcke and Reichenheim found in the plates that came under their observation that the ratio of the displacements of the two maxima was approximately equal to $\sqrt{2}$. This, however, does not seem by any means always to be the case, as the following table, taken from a paper by Stark,[5] of the results obtained by different observers, shows.

RATIO OF DISPLACEMENTS OF THE TWO MAXIMA.

	Observer.
1·75	Stark and Steubing
1·65	Paschen
1·58	„
1·50	Stark and Steubing
1·63	Paschen

[1] "Ann. der Phys.," 23, p. 247, 1907.
[2] *Ibid.*, 28, 978. [3] *Ibid.*, 31, 890, 1910.
[4] "Verh. d. Deutsch. Phys. Ges.," 12, p. 414, 1910.
[5] *Ibid.*, 12, p. 711, 1910.

	Observer.
1·45	Strasser
1·40	,,
1·37	Stark and Steubing.

The photographs taken of the positive rays under electric and magnetic forces show also that in certain cases the velocities of the particles are grouped round certain values, for we find that some of the parabolas have a very decided beaded appearance: each bead corresponds to a group of particles moving with pretty nearly the same velocity. An example of this is shown in Fig. 17, Plate I. The intensity curve corresponding to the Döppler effect ought to have the same type of variations in intensity as these parabolas, and a beaded parabola ought to give rise to a Döppler curve with as many maxima as there are beads on the parabola. Sometimes these beads on the parabolas are quite numerous.

It is remarkable that the parabola corresponding to the atom of hydrogen is often beaded in such a way that the velocity of the particles producing one bead is to that producing the other as $\sqrt{2} : 1$. Thus to explain the maxima in the Döppler curve with displacements in this proportion it is not necessary to assume that the molecules give out the same spectrum as the atom. The occurrence of singly charged atoms of hydrogen with velocities in this proportion of $\sqrt{2}$ to 1 might be accounted for in some such way as the following: the atoms with the larger velocity have been charged atoms during the whole of their career; they were atoms before they passed through the cathode and continue in this state after emerging from it; the atoms with the smaller velocity were part of a charged molecule before passing through the cathode; the molecule would only acquire a velocity $1/\sqrt{2}$ that of the atom. After passing through the cathode and before being deflected by the electric and magnetic fields this charged mole-

cule breaks up into two atoms, one with a positive charge while the other is uncharged.

The Döppler effect we have been considering is that shown by the "series spectrum" of hydrogen. In addition to this spectrum hydrogen gives a second spectrum containing a great number of lines, and this spectrum is developed, though not so brightly as the series spectrum, when positive rays pass through hydrogen. Stark [1] has shown, and his results have been confirmed by Wilsar,[2] that the lines in the second spectrum of hydrogen do not show the Döppler effect with the positive rays. We infer from this that the second spectrum of hydrogen is not due to any of the constituents of the positive rays. This result illustrates the importance of this method for questions relating to the origin of spectra.

Another illustration of this is the case of oxygen. Oxygen gives a series spectrum, a spark spectrum which has not been resolved into series, and some banded spectra. All these spectra are emitted when oxygen positive rays pass through oxygen, the spark spectrum being the brightest. With oxygen it is the spark lines that show the Döppler effect. Wilsar and Paschen could not detect any such effect with the series lines. Stark, however, who used very large dispersions, found the effect in some of the lines; the intensity of the displaced lines was, however, very small compared with that of the undisplaced lines, while in the spark lines the displaced intensity [3] is quite comparable with the normal intensity.

Nitrogen has a line spectrum which has not been resolved into series, and some banded spectra. The line spectrum and one of the banded spectra are found where nitrogen positive rays go through nitrogen; the banded spectrum does not show the

[1] Stark, "Ann. der Phys.," 21, p. 425, 1906.
[2] "Ann. der Phys.," 39, p. 1251, 1912.
[3] Paschen, "Ann. der Phys.," 23, p. 261, 1907.

Döppler effect. Some of the lines in the line spectrum show it very distinctly, while it is quite absent from others (Herman, Wilsar). A very interesting point about the effect in nitrogen is that even for those lines which show the effect the value of $\Delta\lambda/\lambda$ is not constant. Wilsar gives the following table for the Döppler effect for some of the nitrogen lines :—

Wave Length.	$\Delta\lambda/\lambda$
5002·9	11·4
4643·4	10·35
4630·9	10·14
4530·3	10·60
3995·2	6·90

Thus the effect for the line 3995·2 is much less than for any of the others showing that the velocity of the source of this line is considerably less than that of the sources of the others. The different states in which nitrogen occurs in the positive rays are atoms with two charges, atoms with one charge, molecules with one charge, and in exceptional cases atoms with three charges and a tri-atomic molecule with one charge. If the majority of the lines were given out by the doubly charged atom and the line 3995·2 by the singly charged one we should get relative values of $\Delta\lambda/\lambda$, approximately equal to those in the preceding table.

Stark's experiments have shown that the source of the series lines is one of the constituents of the positive rays: the question is, which constituent. We have seen that in hydrogen, for example, we have positively and negatively charged atoms, as well as neutral ones: we have also positively charged and neutral molecules. There is considerable difference of opinion as to which of these is responsible for the series lines in the hydrogen spectrum. All theories concur in regarding the atom and not the molecule as the source of these lines, but

[1] "Phys. Zeit.," 7, p. 568, 1906.

according to Wien's theory the atom radiates when in the neutral state, while Stark maintains that the radiation is emitted when the atom has a positive charge: according to his view the lines emitted by the neutral atom are far away in the ultra-violet.

The pressures at which spectroscopic observations have been made are so high that an atom is continually passing backwards and forwards between the neutral and charged conditions. It is thus a matter of great difficulty to determine whether the atom emits the lines in one state or the other, and there is, I think, at present no experiment which is absolutely decisive between the two views. Thus, for example, it is found that the Döppler effect is increased when the positive rays are exposed to an accelerating potential after passing through the cathode. This, however, does not prove that the particles are charged when giving out the light, for the particles which are uncharged at one time have at other times a positive charge and so would be accelerated.

Perhaps the strongest argument in favour of the radiating particles being positively charged is that in certain cases, as Reichenheim has shown, the anode rays (see p. 84) show the Döppler effect, but even this is not conclusive, as some of the positively charged particles might have been neutralized after they had acquired their high velocity under the electric field.

There is another view as to the origin of the radiation which explains in a simple way some of the characteristic properties of the Döppler effect: this is that the light is given out by particles which have just been neutralized by union with a negatively electrified corpuscle. The corpuscle falls into the positively charged atom and the energy gained by the fall is radiated away as light. On this view the intensity of the light should vary with the number of recombinations of positive ions and negative corpuscles. Let n be at any

instant the number of neutral particles per unit volume moving with velocity V, p the number of positive particles moving with the same velocity, N the number of corpuscles in the tract of these particles per unit volume.

Then the number of recombinations per second will be

$$p\mathrm{N}f(v)$$

when $f(v)$ is a function of v which will vanish when v is very large, for recombination will not take place if the relative velocity of the positive particle and the corpuscle exceeds a certain value.

The number of neutral particles ionized per second will be

$$n\mathrm{N}\mathrm{F}(v)$$

where $\mathrm{F}(v)$ is a function of v which vanishes when v is very small, for if the particle is to be ionized by a collision the relative velocity of the particle and corpuscle must exceed a critical value.

When the composition of the beam of positive rays has become steady the number of ionizations must equal the number of recombinations, hence

$$p\mathrm{N}f(v) = n\mathrm{N}\mathrm{F}(v)$$

and therefore

$$= \frac{(p+n)\mathrm{N}f(v)\mathrm{F}(v)}{f(v)+\mathrm{F}(v)}$$

Since $f(v) = 0$ when $v =$ infinity and $\mathrm{F}(v) = 0$ when $v = 0$, $f(v)\mathrm{F}(v)$ will have a maximum for a certain value of v which will not however depend on the potential difference between the electrodes in the discharge tube. The factor $p+n$, the total number of positive rays charged or neutral whose velocity is v, will also be a function of v and this function will depend upon the value of E, the potential difference between the electrodes in the discharge tube, for evidently if E increases, the value of v for which $p+n$ is a maximum will increase too.

On the view we are considering, the intensity of the light showing a Döppler effect corresponding to the value v will be

proportional to the number of recombinations of positive ions moving with this velocity with negatively electrified corpuscles. It will thus be proportional to $\beta N f(v)$ which we have seen is equal to

$$(\beta + n)\left\{\frac{f(v)F(v)}{f(v)+F(v)}\right\}N$$

The second factor in this expression

$$\frac{f(v)F(v)}{f(v)+F(v)}$$

has its maximum value for a value of v which does not depend upon the potential difference: the other factor $(\beta + n)$ does depend upon this potential difference. Thus the value of v for which the product of these factors is a maximum will depend to some extent on E, but since the value of v which makes one of the factors a maximum is quite independent of E we should expect that the variation with E of the velocity which makes the product a maximum would be smaller than the variation in the average velocity of the particles in the positive rays.

Again since $F(v)$ vanishes when v is less than a certain value v_0 there will be no light showing a Döppler effect corresponding to a velocity less than v_0, thus there will be a dark space between the original line and the displaced lines. This also is in accordance with the observations. Since $f(v)$ vanishes when v is greater than a certain value v, there will be no Döppler effect showing a greater displacement than that corresponding to v. Though it has not perhaps been absolutely proved there are strong indications that the Döppler effect cannot be increased beyond a certain definite value, however large the potential applied to the discharge tube may be.

The spectroscopy of the positive rays suggests some very interesting questions, as, for example, what kind of light do the

molecules emit? In the positive rays in hydrogen the molecules frequently outnumber the atoms, but no radiation that can be attributed to the molecules has yet been detected. The second spectrum of hydrogen is there, but as it does not show the Döppler effect it cannot be due to the molecules. It would seem as if the molecules must either give rise to a continuous spectrum or else to one in the infra red.

As the second spectrum of hydrogen is present when the positive rays pass through a gas, but does not show any displacement, it must arise from some process in which the moving particles do not take part, such for example as the combination of a positive atom with a negative one (not with a corpuscle) to form a neutral molecule.

Stark[1] has detected by the increased Döppler effect lines due to the doubly and triply charged atoms of mercury and to the doubly charged atom of helium. He finds that the lines given out by the multiply charged atoms belong to different series in Paschen and Runge's classification from those given out by atoms with only one charge.

When positive rays produced in a gas A pass through a gas B the spectra of both A and B are given out: Wilsar, "Phys. Zeitschr.," 12, p. 1091, and Fulcher (*ibid.* 13, p. 224), have shown that all the lines of A are displaced while all those of B are in their normal position. A bibliography of the Döppler effect in the Positive Rays has recently been published by Fulcher, "Jahrb. d. Radioaktivität," X, p. 82, 1913.

SPECTRA PRODUCED BY BOMBARDMENT WITH POSITIVE RAYS.

The spectra produced when the positive rays strike salts of the alkali metals are very interesting. The salts give

[1] "Ann. der Phys.," XL, p. 499, 1913; XLII, p. 241, 1913.

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out the lines of the alkali; for example Li Cl give out the red lithium line and sodium salts the D line. It is remarkable that the lines due to the metal are more easily excited in the salts than in the metal themselves. Thus if the liquid alloy of sodium and potassium is bombarded by positive rays the specks of oxide on the surface glow brightly with the sodium light while the clean surface remains quite dark. Some observers have noticed what seems a similar effect with hydrogen, viz. that the hydrogen lines are more easily excited in water vapour than in pure hydrogen. The fact that in the positive ray photographs, the parabolas corresponding to a certain type of ray, for example the carbon or oxygen atom with two charges, is more easily developed from compounds than from the molecules of the gases themselves is probably connected with this effect.

The production of spectra by bombardment with cathode rays has been investigated by Gyllensköld ("Ark. f. Math. Ast. oet. Fys.," 4, No. 33, 1908), and by Stark and Wendt ("Ann. der Phys.," 88, p. 669, 1912) who have shown that the colourless salts of the alkalies and alkaline earths and also of thallium, zinc, and aluminium give out the series lines of the metal when struck by the positive rays and that the lines given out do not depend upon the character of the salts. According to Stark and Wendt the seat of the emission is not the surface of the salt itself but a layer of gas, less than 1 mm. thick, close to the surface. This layer is analogous to the velvety glow which covers the surface of the cathode where an electric discharge passes through a gas at a low pressure.

To develop the spectrum of the metal the positive rays must have more than a certain critical amount of energy depending on the nature of the salt. The values of V, this critical energy, measured by the number of volts through which the atomic charge must fall to acquire it, have been

measured by Stark and Wendt and are given in the following table:—

Metal.	Salt.	Light given out.	V.
Lithium	chloride	red	600
,,	oxide	red	600
	,,	λ 6710	<800
Sodium	chloride	yellow light	750
Potassium	chloride and oxide	λ 580	<2400
Rubidium	sub-oxide	λ 572	<3500
Cæsium	chloride	λ 566	<4500
Magnesium	chloride	λ 518	<1200
Calcium	fluoride	red violet light	150
	carbonate	,,	1500
	sulphate	,,	1500
	oxide	,,	1400
Strontium	chloride	λ 496	<2500
Barium	,,	λ 554-493	<2500
Thallium	sulphate	λ 535	4500
Aluminium	oxide	λ 396	<4500
Zinc	,,	λ 475	<4600

It must not be supposed that the amounts of energy given in the last column represent the minimum amount required to excite the particular kind of light given in the third column. When energy has to be transferred from a charged atom to a corpuscle, the latter only receives a very small fraction of the energy of the atom, thus a very small fraction of the energy of the positive rays may be transformed into a kind available for light production.

Gyllensköld observed that in addition to the D lines sodium chloride gives out a series of bands in the blue and Stark and Wendt have shown that for this to occur the energy of the rays must exceed a critical value which in most cases is less than that required to excite the line spectrum.

DISINTEGRATION OF METALS UNDER THE ACTION OF POSITIVE RAYS.

When positive rays strike against a metallic surface, the metal disintegrates and forms a deposit on the walls of the

tube surrounding the metal. A well-known instance of this is the "spluttering" of the cathode in a vacuum tube; another is observed when working with an apparatus like that shown in Fig. 10; after long use the thin metal tube which passes through the cathode gets worn away at the end nearest the discharge tube, as if it had been struck by a sand blast. Sometimes several millimetres of the tube are destroyed in this way. An excellent account of the very numerous experiments which have been made on the spluttering of the cathode will be found in a report by Kohlschütter ("Jahrbuch der Radioaktivität," July, 1912).

The experiments of Holborn and Austin, Granquist, and Kohlschütter indicate that with a constant current w the loss of weight in a given time may be represented by a formula of the type

$$w = \alpha \frac{A}{n}(V\text{-}S)$$

where V is the cathode fall of potential, A the atomic weight of the metal, n a small positive integer, and α and S quantities which are much the same for all metals, or at any rate the metals can be divided into large classes and α and S are the same for all the metals in one class. For a current of ·6 milliamperes, Holborn and Austin found that for all the metals they tried S was 495 volts. We see that a formula of this type implies that there is no spluttering unless the cathode fall of potential exceeds a definite value S and this seems to be verified by experience.

The experiments of Holborn and Austin, Kohlschütter and others have shown that this expression for the loss of weight of the cathode fails when V exceeds a certain value, for hydrogen this value seems to be so low that the expression fails before the loss of weight becomes measurable.

The loss of weight of the six metals Al, Fe, Cu, Pt, Ag,

Au have been measured by Kohlschütter and Müller ("Zeitschr. f. Elektroch.," 12, 365, 1906) and Kohlschütter and Goldschmidt (*ibid.* 14, 221, 1908) in the gases H_2, He, N_2, O_2 and Au, under as nearly as possible identical electrical conditions. They found that for all gases the amount of weight lost was in the order in which the metals are written above, gold always losing the greatest amount and aluminium the least. For the same metal in different gases the loss of weight followed the order of the atomic weight of the gases, the loss in hydrogen being least and that in argon greatest. This may be connected with the fact that (see p. 47) elements of high atomic weight acquire multiple charges of electricity more easily than the lighter elements, and atoms with a multiple charge have more energy when they strike against the cathode than those which have only one charge. It is easy to understand in a general way why particles with the large amount of energy possessed by the positive rays when they strike against an atom in the cathode might communicate to it sufficient energy to enable it to escape from the cathode. A complete theory, however, is lacking, and one which would explain some of the more striking facts, such as why the value of S is so nearly the same for metals of very different physical and chemical properties, would probably throw a good deal of light upon some important properties of the atom.

Dechend and Hammer ("Zeitschr. f. Elektroch.," 17, 235) allowed the positive rays produced in sulphuretted hydrogen to pass through a perforated cathode and after deflection by magnetic and electric fields to fall upon a plate of polished silver, they could detect the parabolas on the plate, but while the parabolas due to hydrogen were so faint that they could only be detected as breath figures, those due to the heavier atoms, presumably sulphur, had so affected the plate that they could not be removed either by acid or rubbing. The great-

est effect, however, was produced by the undeviated rays. In addition to the effects produced when the positive rays strike against a metal plate there is, as Schmidt has shown, a general oxidation over the surface when the metal is oxidizable and when the gas surrounding it contains oxygen. The passage of the positive rays through the oxygen produces atomic oxygen which is very active chemically and which attacks the plate. If, on the other hand, an oxidized plate is placed in hydrogen and exposed to the action of positive rays the oxide is reduced, the rays produce atomic hydrogen which acts as a strong reducing agent.

Some of the atoms constituting the positive rays seem to enter a metal against which they strike, and either combine with the metal or get absorbed by it. Helium, neon, and mercury vapour seem especially noticeable in this respect. If a cathode has once been used for any of these gases, positive rays corresponding to these elements will be found when the cathode is used with other gases, and it requires long continued discharge and repeated fillings with other gases before they are eliminated.

A very valuable Bibliography of Researches on Positive Rays has been published by Fulcher (Smithsonian Miscellaneous Collection, 5. p. 295, 1909).

ON THE USE OF THE POSITIVE RAYS FOR CHEMICAL ANALYSIS.

1. We shall now proceed to show how the method of positive rays supplies us with a very powerful method of chemical analysis, and how from the study of the positive ray photographs we are able to determine the different kinds of atoms and molecules in the discharge tube. Each atom or molecule in the discharge tube produces a separate parabola on the photographic plate and if we measure these parabolas then by means of the formula

$$\frac{e}{m} = \frac{y^2 A}{x B^2}$$

we can determine the value of e/m for the particles producing any of the parabolas which occur on the photographic plate. We know, too, that the charge e is either the ionic charge, whose value on the electrostatic system of units is $4{\cdot}8 \times 10^{-10}$, or some multiple of it. We have, too, as we shall see, the means of determining what this multiple is. As we can determine the value of e and since we know by the measurement of the parabola the value of e/m we can deduce the value of m and thus determine the masses of the particles forming the positive rays. As these particles are the atoms and molecules of the gases in the discharge tube it is evident that in this way we can determine the atomic or molecular weight of the gases in the positive rays. We can thus identify these gases as far as can be done by the knowledge of their atomic weight. The study of the photographs gives us in fact the atomic

weights of the various gases in the tube and thus enables us to determine the nature of the contents of the tube. We can thus analyse a gas by putting a small quantity of it into a discharge tube and taking a photograph of the positive rays. This method of analysis has many advantages. In the first place only a very small quantity of gas is required, the total amount of gas in the discharge tube of the size described on page 16 would only occupy about ·01 c.c. at atmospheric pressure and a constituent present to the extent of only a very small percentage would give well defined parabolas. If there is a new gas in the tube it is indicated by the presence of a new parabola, but this parabola does far more than show that something new is present, it tells us what is the atomic weight of the new constituent. Let us compare for a moment the method with that of spectrum analysis. We might detect a new gas by observing an unknown line in the spectrum when the electric discharge passed through the gas. This observation would, however, tell us nothing about the nature of the substance giving the new line, nor, indeed, whether it arose from a new substance at all: it might be a line given out by a well-known substance under new electrical conditions. Again, if a substance is only present to the extent of a few per cent it very often happens that its spectrum is completely swamped by that of the more abundant substance: thus, for example, in a mixture of helium and hydrogen we cannot observe the helium lines unless the helium is a considerable percentage of the mixture.

This is not the case with the positive rays, or at any rate not to anything like the same extent; the presence of one per cent of helium would be very easily detected by the positive rays. The method, too, is more sensitive than that of spectrum analysis. With the apparatus described above the helium in 1 c.c. of air, i.e. about 3×10^{-6} c.c., could be detected with great

ease even when it formed only about one per cent of the mixed gases in the tube. No special attention was paid to making this particular apparatus specially sensitive. To get the best results the size of the tube running through the cathode has to be chosen with reference to the distance of the photographic plate from the cathode, and other circumstances; this was not done in the apparatus under discussion, nor were the photographic plates used of any special sensitiveness; by attention to these points the sensitiveness of the method could very materially be increased.

Again the method of the positive rays enables us when we have found the substance to say whether the molecule is monatomic or diatomic; if it is diatomic we shall have two new parabolas, one indicating particles with a mass twice that of the picartles producing the other; if the molecule is monatomic there will be only one parabola unless the particle acquire a double charge and the presence of this extra charge can be recognized by the tests previously described. The method of the positive rays has the advantage of revealing the presence of the molecules of compound gas as well as the atoms and molecules of elementary substances. Since different compounds may have the same molecular weight there is sometimes ambiguity in interpreting the photographs produced by the positive rays; for example, CO_2 and N_2O produce the same parabolas as also do CO and N_2. In such cases to find out the origin of such a parabola we must repeat the experiment under different conditions; for example, if we put something in the tube which absorbs CO_2 and not N_2O and find that the parabola disappears, we conclude that it was due to CO_2; if it does not disappear it is not due to CO_2, but to N_2O or some other compound with the same molecular weight.

2. The ambiguity as to whether a line with a value of m/e equal say to 8 (m/e for the hydrogen atom being taken

as unity) is to be ascribed to an atom with atomic weight 8 carrying a single charge or to one with an atomic weight 16 carrying two charges or to one with atomic weight 24 with three charges may be removed by the considerations given on page 47. For example, if the particle producing this parabola A carries a double charge there will be another and more intense parabola B for which the value of e/m is twice that for A, and the parabola B will have a prolongation towards the vertical axis, the distance of the head of this prolongation from the vertical axis being half the distance of the heads of the normal parabolas (see p. 47). If A represents a particle with a threefold charge there will be another stronger parabola B for which e/m has three times the value corresponding to the parabola A, and B will have a prolongation towards the vertical axis extending to one third of the normal distance.

3. For the purposes of Chemical Analysis it is not necessary to use the elaborate apparatus shown in Fig. 10, the simpler one shown in Fig. 6 is all that is required for this purpose. The more elaborate apparatus is only required when we require to know accurately the values of the quantities A and B which occur in the expression for e/m.

For the determination of the masses of the particles producing the different parabolas the measurement of the quantities A and B is unnecessary if we can recognize the particle which produces any particular parabola. For since A and B are the same for all the parabolas, then for any two parabolas we have by the equation on page 106

$$\frac{(e/m)_1}{(e/m)_2} = \frac{y_1^2/x_1}{y_2^2/x_2}$$

when $(e/m)_1$, $(e/m)_2$ are the values of e/m, for the particles producing the parabolas (1) and (2) respectively, (x_1y_1) (x_2y_2) are the co-ordinates of any point on the first and second parabolas respectively.

If the points on the two parabolas have the same values of x so that $x_1 = x_2$
then

$$\frac{(e/m)_1}{(e/m)_2} = \frac{y_1^2}{y_2^2}$$

if the charges are the same

$$\frac{m_2}{m_1} = \frac{y_1^2}{y_2^2}.$$

As the line corresponding to the atom of hydrogen occurs on all the plates and can at once be recognized by being the most deflected line on the plate, the value of (e/m) for the particles producing any parabola can be at once, by the aid of this formula, compared with the value of this quantity for an atom of hydrogen and the masses of the various particles thereby determined.

A convenient instrument for making the necessary measurements is shown in Fig. 14. The plate is inserted in the holder A. The camera is arranged so that the direction in which the rays are deflected by the magnetic force alone (the vertical axis in the preceding figures) is parallel to the longer side of the photographic plate. The deflection due to the electrostatic field is at right angles to this and parallel to the shorter side of the plate. The plate is placed in the holder so that the axis of no electrostatic deflection is parallel to B, and that of no magnetic deflection perpendicular to BB. A needle NN whose point comes close to the plate is placed in the carrier C which can move parallel to BB by sliding along BB, and perpendicular to it by means of the screw S, the position of the carrier is read by two verniers V_1 and V_2. There is always a circular patch of some size on the plate at the place where the undeflected particles hit the plate: the zero is at the centre of the spot. By putting the needle first at the centre of the spot, then moving the carrier through a certain distance perpendicular to BB by the screw S, and sliding the carrier parallel to BB until the

needle comes on the parabolas in turn, the values of y for the different parabolas corresponding to a constant value of x can be measured.

The equation page 110 then enables us to find the ratio of the masses of the particles producing the different parabolas. We can avoid any uncertainty as to the position of the zero by taking two photographs, the electrostatic field remaining the same in the two, while the magnetic field in the first photograph is equal in magnitude but opposite in direction to that in the second. Thus each kind of particle will now give two parabolic arcs, as in Fig. 38, and the distance between two points AB situated on the same vertical line will be twice the vertical deflection due to either magnetic field. As these arcs are much finer than the central spot, the distant AB can be measured with greater accuracy than either deflection separately.

The advantages of the method are illustrated by the photographs reproduced in Figs. 47 and 48, Plate IV. These represent the parabolas obtained when the discharge passes through the residues of liquid air; Fig. 47 represents the curve for the residues which had been treated so as to include the heavier constituents of the atmosphere; Figs. 48, Plate IV. and 49, Plate V. when the treatment had been such as to retain the lighter constituents.

When the plate for the heavier gases is measured up, it shows a faint line corresponding to the atomic weight 128 (xenon), a very strong line corresponding to an atomic weight 82 (krypton), a strong argon line 40, and the neon line 20. There are no lines on the plate which cannot be ascribed to known elements, and hence we may conclude that in the atmosphere there are no unknown gases of large atomic weight occurring in quantities comparable with those of xenon and krypton. This is a good example of the convenience of this method of analysis, for a single photograph reveals at a glance all the gases in the sample analysed. This photograph shows

very plainly the existence of multiply charged atoms of the monatomic gases. The neon parabola extends towards the vertical to within half the normal distance of the heads of the parabolas; this shows that some of the neon atoms carry a double charge, and this is confirmed by the presence of a line on the plate for which e/m has twice the value corresponding to the neon line. The argon parabola approaches the vertical even more closely than that representing neon, as it begins at a distance from the vertical only one-third the normal distance, showing the argon atom can have as many as three charges. The krypton line approaches to within one-quarter of the normal distance showing that the krypton atom may have as many as four charges. We see from this how the maximum charge acquired by atoms of elements belonging to the same group increases with the atomic weight of the element.

Let us now consider the photograph taken with the lighter constituents (Fig. 48, Plate IV.): here we find the line corresponding to helium; to neon, this is very strong and there is also a line corresponding to the neon atom with a double charge; to argon, and in addition there is a line corresponding to an element with an atomic weight 22. A molecule of carbonic acid with a double charge would give a line in this position, but this cannot be the origin of the line as the carbonic acid can be removed from the gas without producing any change in the brightness of the line. This line is much fainter than the neon line so that in the atmosphere the quantity of the gas which is the source of this line is small compared with that of neon.

The origin of this line presents many points of interest: there is no recognized element with this atomic weight, nor are there any compounds of recognized elements which would satisfy these conditions. It must, I think, be a new element.

For though the compound NeH_2 would have the required mass, there is strong evidence that the line is due to an element. Thus we find on the plate another line for which $m/e = 11$, and the line for which $m/e = 22$ has a prolongation half way to the axis, showing that the particle exists with a double charge; this is a frequent occurrence with an atom of an element but I do not know of any case of a molecule of a compound possessing more than one charge.

If we accept Mendeleef's table there is no room for an element with such an atomic weight as 22 unless we suppose that near neon we have a group of two or more elements with similar properties, just as in another part of the table there is the group iron, nickel, and cobalt.

Mr. F. W. Aston has made at the Cavendish Laboratory many attempts to separate this new gas from neon whose atomic weight is 20. The method he first tried was to fractionate a mixture of the two gases by means of their absorption by cocoanut charcoal cooled by liquid air. This absorption in the case of most gases increases with the atomic weight, and though the difference between 20 and 22—the atomic weights of the two gases in the mixture—is but small, he devised an apparatus by means of which the absorption was repeated so frequently that if there had been as great a difference in the absorption as from the analogy with other gases we might have expected from the difference in their atomic weights, the proportion between neon and the new gas would have been appreciably altered by the treatment. He could, however, find no difference whatever in this proportion before and after fractionation. To measure this proportion he used two methods, (1) by comparing the intensity of the two lines in the positive ray photograph and (2) by measuring the density of the mixture by means of a specially constructed quartz balance which would have detected an alteration of very few

per cent in the proportion between the two gases. We conclude, therefore, that the physical properties of the two gases are much more nearly equal than we should have expected from their atomic weights.

Another method of fractionation used by Mr. Aston was more successful, this was to allow the mixed gases to diffuse through a porous substance such as the stem of a clay tobacco pipe. The lighter constituent diffuses faster than the heavier one and by this means he obtained sufficient alteration in the proportion between the two gases to produce appreciable changes in the relative brightness of the two lines on the positive ray photograph, and changes in the density large enough to be detected by the quartz balance. No difference, however, could be observed in the spectrum of the mixture, and this in conjunction with the failure of the cooled charcoal to produce any separation gives some grounds for the suspicion that the two gases, although of different atomic weights, may be indistinguishable in their chemical and spectroscopic properties. There are several products of radio-active transformations such as radio-lead and thorium which have different atomic weights and are supposed to be inseparable from each other by any chemical process.

As another example of the method we will take its application to the investigation of the gases given off when solids are bombarded by cathode rays. The apparatus used for this is shown in Fig 13. B is the vessel in which the positive rays are produced. A is a vessel communicating with B by two tubes, one of which is a very fine capillary tube while the other is 5 or 6 mm. in diameter ; taps are inserted so that one or both of these tubes may be closed and the vessels isolated from each other. The vessel A contains a curved cathode such as are used for Röntgen ray focus tubes, and the cathode rays focus on the platform on which the substance to be bombarded is

PLATE V.

FIG. 49.

The line corresponding to the element with atomic weight 22 can be seen just under the neon line which is the strong line on the top at the right hand side.

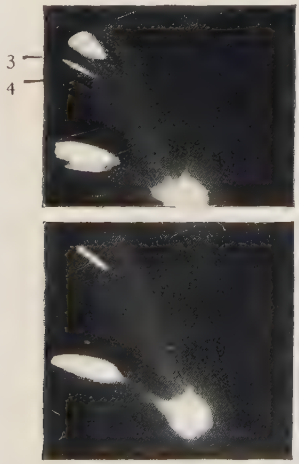

FIG. 50.

placed. After the metal or other solid under examination has been placed on the platform, the taps between A and B are turned and A is exhausted by a Gaede pump until the vacuum is low enough to give cathode rays. The electric discharge is then sent through A and the solid on the platform bombarded. The result of the bombardment is that in a few seconds so much gas, mainly CO_2 and hydrogen, is driven out of the solid that the pressure gets too high for the cathode rays to be formed, and unless some precautions to lower the pressure were taken the bombardment would stop. To avoid this a tube containing charcoal cooled by liquid air is connected with A, the cooled charcoal absorbs the CO_2 and enough of the hydrogen to keep the vacuum in A low enough to give cathode rays.

To see what gases are given off in consequence of the bombardment, a photograph of the positive rays is taken when the connexion between A and B is cut off. After this is finished, and when the bombardment has gone on for several hours, the taps between A and B are turned and the gas from A is allowed to go into B; another photograph is taken. The lines in the second photograph which are not in the first represent the gases which have been liberated from the solid by the bombardment with cathode rays. Fig. 50, Plate V., represents two such photographs; (*a*) that taken before turning the tap and (*b*) after. In (*b*) there are the following lines which do not occur in (*a*): (1) a very strong line corresponding to a substance with atomic weight 3; (2) one corresponding to helium, atomic weight 4, generally much fainter than the 3 line, and (3) lines representing neon with one and two charges. The amount of helium and neon are so small that their spectral lines were not visible when the discharge through the tube was examined with the spectroscope. Nearly every substance I have tried, including platinum, palladium, aluminum, copper,

zinc, iron, nickel, silver, gold, lead, graphite, diamond dust, lithium chloride, two specimens of meteorites and a large number of metallic salts, give out, when first they are bombarded, helium as well as the substance giving the 3 line; the amount of helium given off generally falls off very considerably after the bombardment has been prolonged some hours; the substance giving the 3 line is, however, much more persistent, and in some cases, for example that of KHO, the bombardment may be prolonged for several weeks without any diminution in the rate of evolution of the gas.

The presence of mercury vapour in the vessel A diminishes very much the intensity of the 3 line; hence we may conclude, I think, that the substance which gives the 3 line combines with mercury vapour when an electric discharge passes through a mixture of the two gases. Another case where the presence of one gas causes the disappearance of the lines due to another is that of oxygen and mercury vapour; the mercury lines are not seen in the photographs of the positive rays when the gas in the tube is mainly oxygen, although with most gases these are about the strongest lines on the photographic plate. The disappearance of the mercury lines in this case may easily be explained by the combination of the mercury vapour with the oxygen.

ON THE NATURE OF X_3 THE SUBSTANCE GIVING THE "3" LINE.

The only known substances which could give the line with the value of m/e three times that of the hydrogen atom are: (1) an atom of carbon charged with four units of electricity, and (2) a molecule containing three atoms of hydrogen. The first of these alternatives must be abandoned for the following reasons: (1) we have seen that a line corresponding to a

multiple charge on an atom is accompanied, unless the pressure is exceedingly low, by certain peculiarities in the line corresponding to the atom with one charge; for example, if there were a line corresponding to a carbon atom with two charges, the line corresponding to the carbon atom with one charge would be prolonged until its extremity was only one-half the normal distance from the vertical axis; if there were a line corresponding to the carbon atom with three charges, the ordinary carbon line would be prolonged until its distance from the vertical was only one-third of the normal distance, while a carbon atom with four charges would prolong the ordinary carbon line to within one-quarter of the distance from the axis. Again the greater the charge the less the intensity, so that a line due to a quadruply charged carbon atom would be accompanied by a stronger line due to a triply charged atom, a still stronger one due to a doubly charged atom, while the normal carbon line would be the strongest of all.

Now in the case of the 3 line we do not find any of these characteristics; the carbon line is not prolonged to within one-quarter of the normal distance, and so far from the line being accompanied by a stronger line due to a doubly charged carbon atom, in many of the cases where the 3 line is strongest the line due to the doubly charged atom is not strong enough to be detected; indeed in some of these cases the 3 line is stronger than the normal carbon line.

Again since the gas giving the 3 line can be stored in the vessel A for days after the bombardment has ceased, if this line were due to carbon with four charges it must be because some carbon compound is formed by the bombardment, which when introduced into the discharge tube gives, when the discharge passes through it, carbon atoms with four charges. Now experiments have been made with a great variety of carbon carbons introduced directly into the discharge tube, CH_4, CO_2,

CO, C_2H_4, C_2H_2, $COCl_2$, CCl_4, and many others, and none of these have given this line: we must therefore abandon this solution of the problem.

I find too that whenever large amounts of X_3 are produced spectroscopic examination shows that considerable quantities of hydrogen are liberated by the bombardment; in fact the brightness in the spectroscope of the hydrogen lines in the bombardment vessel may be taken as giving a rough indication of the brightness to be expected of the X_3 line in the positive ray photograph.

Let us next consider the connexion between the production of X_3 and the nature of the substance bombarded by the cathode rays. We get more definite conditions for the bombarded body if we use soluble salts instead of pieces of metal or minerals. The latter may have absorbed X_3 and contain stores of this gas in the absorbed state which are liberated when the solid is bombarded by cathode rays. If we could subject the solid before the bombardment to some process by which we could free it from absorbed gas we should expect that if the source of the X_3 were gas absorbed by the solid, the bombardment of a substance which had been treated in this way would not give rise to any X_3.

The most effective way of liberating the absorbed gas would seem to be to dissolve the solid in a suitable solvent and then evaporate the solution to dryness. Those salts which are soluble in water or alcohol can readily be treated in this way. I have therefore made experiments on a large number of soluble salts bombarding them before and after they have been dissolved and evaporated to dryness, and testing by the positive ray photographs the yield of X_3 in each case. Sal-ammoniac made by allowing streams of ammonia and hydrochloric acid gas was found to give X_3 when bombarded; in this case the possibility that X_3 was absorbed in the salt would seem to be excluded.

I find that salts may be divided into two classes with respect to the way in which their evolution of X_3 is affected by solution and evaporation. One class of salts which includes KI. Li_2CO_3. KCl give a very much smaller output of X_3 after this treatment than they did before; the other class which includes KOH, LiCl, LiOH, $CaCl_2$ give much the same output after solution as they did before even though they are dissolved and evaporated over and over again. The salts of the first class do not contain hydrogen, while those of the second either contain hydrogen or are deliquescent and thus can absorb water from the atmosphere on their way to the bombardment chamber after evaporation. The fact that some salts continue to give supplies of X_3 after repeated solution and evaporation shows I think that X_3 can be manufactured from substances of definite chemical composition by bombardment with cathode rays, and the fact that such salts contain hydrogen either as part of their constitution or in water of crystallization suggests that X_3 consists of hydrogen and is represented by the formula H_3. The other alternative is that it is an element produced by the disintegration of some or other of the elements in the salt, but this view would not explain why its production is so closely associated with the presence of hydrogen.

One of the most convenient ways of preparing X_3 is to bombard potash, KOH, by cathode rays. I bombarded a few grammes of potash for several months pumping off after each day's running the gases liberated by the bombardment, these consisted of H_2. O_2 and X_3 and at the end of the time I could not detect any falling off in the rate of production of X_3. By bombarding the potash, supplies of X_3 mixed with hydrogen and oxygen were obtained and a series of experiments made with them with the object of discovering some of the properties of this gas. The method used to test for the

presence of X_3 after the mixed gases of which it was a constituent had been subjected to any treatment was to introduce a small quantity of the mixed gases into the discharge tube, take a positive ray photograph and estimate the brightness of the X_3 line. Before such experiment the discharge tube was well washed out with oxygen and a test photograph taken to make certain that no X_3 was in the tube before the introduction of the gas which was to be tested. One property of this gas, that of combining with mercury vapour when an electric discharge passes through a mixture of these gases, has already been mentioned. Another property was discovered accidentally: the mixed gases obtained by bombarding the potash were drawn off day by day and stored up for further tests. It was soon noticed that some of the samples kept much better than others and it seemed possible that this difference might be due to differences in the brightness of the light to which the samples had been exposed. To test this a piece of magnesium wire was burnt in front of a sample which was known to contain a considerable quantity of X_3, with the result that the X_3 almost disappeared. The gas exposed to the light was a mixture of hydrogen, oxygen and X_3, if the oxygen is taken out of the mixture by absorbing it with charcoal cooled with liquid air, exposure to light produces no effect on the X_3; the conclusion we draw is that under the influence of the light the X_3 combines with oxygen. If the mixture is kept in the dark or if the oxygen is taken out of it the X_3 lasts for a long time, certainly for several weeks. Again if a strong spark is sent through the mixture containing oxygen so that a vigorous explosion takes place the X_3 disappears, presumably combining with the oxygen. If the oxygen is removed the mixture of hydrogen and X_3 will stand a good deal of sparking without any considerable diminution in the amount of X_3.

The fact that sparking with oxygen destroys the X_3, makes

the removal of the hydrogen, which is by far the largest constituent of the mixture, a matter of considerable difficulty. The most effective way I know of increasing the proportion of X_3 is first to remove the oxygen, then to put the mixture of H_2 and X_3 into a vessel to which a palladium tube is attached ; when the palladium is heated to redness the hydrogen diffuses through it much more rapidly than the X_3, though some of this gas can get through the palladium. The result is that the gas left behind in the vessel contains a much greater proportion of X_3 than it did before. The preponderance of H_2 in the original mixture is, however, so great that even by this means I have not been able to prepare any sample in which the hydrogen was not greatly in excess.

Another interesting property is that the X_3 almost disappears when placed in a quartz tube with some copper oxide and the whole heated to a red heat.

In the absence of oxygen and copper oxide X_3 may be heated to a high temperature without destruction. Summing up the results we see that when hydrogen is present in the substance bombarded a continuous supply of X_3 can be obtained, while from substances which do not contain hydrogen the supply is soon exhausted. Again, under certain conditions such as exposure to bright light, vigorous sparking in the presence of oxygen, contact with glowing copper oxide, X_3 combines with oxygen. These results seem to me to point to the conclusion that X_3 is tri-atomic hydrogen H_3. If this is so, its properties are very interesting. Unlike O_3 its existence cannot be reconciled with the ordinary views about valency. If, however, we regard an atom of hydrogen as consisting of a positive nucleus and one negative corpuscle, it will exert forces analogous to those excited by a magnet and I can see no reason why a group of three of these arranged so that their axes form a closed ring should not form a stable arrangement.

The stability of X_3 is much greater than that of ozone O_3, the latter does not persist for nearly as long as X_3, it breaks up at a moderate temperature which would have no effect on X_3, and it disappears under a kind of sparking which would leave X_3 undecomposed. In fact X_3 seems more stable than any known allotropic form of an element.

Many attempts have been made to obtain spectroscopic evidence of X_3 by putting mixtures of this gas and hydrogen in a quartz tube and photographing the spectrum obtained when a discharge was sent through the tube, the electrodes were pieces of tin-foil placed outside the tube. No lines which could be ascribed to X_3 were detected, the first and second spectra of hydrogen were bright, and in spite of efforts to get rid of mercury vapour the mercury lines were visible.

Bombardment by cathode rays is not the only method of obtaining X_3. I heated by an electric current in a good vacuum a fine tantalum wire, such as are used for metallic filament lamps, until it fused and found that a considerable amount of X_3 was given off. Some time ago I found that when the discharge from a Wehnelt cathode was sent through an exhausted tube X_3 was liberated. I have found subsequently that it is not necessary to send the discharge through the tube, the heating of the cathode is sufficient to liberate this gas. Again if a considerable quantity of potash is placed in a vacuum and left for some time an appreciable quantity of X_3 is liberated.

EVOLUTION OF HELIUM AND NEON.

I have examined by the positive ray method the gases given off by a great variety of substances when they are bombarded by cathode rays,—the substances include most of the metals, a considerable number of minerals, and many metallic salts,—

and have found in almost every case when cathode rays had a high speed that traces of helium were present in the gases liberated in this way. The rate of evolution of helium is generally considerably greater at the commencement of the bombardment than when this has been prolonged for some time, but in the majority of cases there seems to be a residual effect which remains even when the bombardment has lasted for a long time. The larger effect observed at first is due I think to helium absorbed by, or accumulated on, the substance bombarded ; the question arises, is the more lasting evolution of this gas due to the liberation of accumulated helium lingering in the solid, or are the atoms of the elements bombarded by the cathode rays disintegrated, one of the products of disintegration being helium, or as a third alternative are there salts of helium present in the substance as impurities, and are these dissociated by the cathode rays. The first published account of the evolution of helium in vacuum tubes is that given by Sir William Ramsay ("Nature," July, 18, 1912) ; he found that when the glass of old Röntgen ray bulbs was heated, sufficient helium was given off to be detected by spectroscopic methods.

Before proceeding to consider how the various explanations of the appearance of helium may be tested, it is advisable to discuss some general aspects of the question. The difficulty of finding the origin of the helium is considerably greater than the corresponding problem for X_3 owing to the presence of helium in the atmosphere. The positive ray method is so sensitive that the amount of helium in a cubic centimetre of air (which according to Ramsay is about 4×10^{-6} c.c. at standard temperature and pressure) produces a strong line on the photograph, a line stronger than that found in most of the experiments described below, so that in the greater part of these experiments we are dealing with amounts of helium less

than that which could be accounted for by the entrance of 1 c.c. of air into the apparatus. This source of helium has to be carefully guarded against; it is necessary, for example, to be very careful in the use of charcoal cooled by liquid air for producing the final vacuum. The cooled charcoal hardly absorbs the helium at all and thus this gas is not taken out of the vessel by this method of exhaustion. For example, if the first stages of the exhaustion were done by a water pump which takes the pressure down to a centimetre or so, and the rest of the exhaustion done by cooled charcoal, sufficient helium and neon would be left in the vessel to give very strong lines on the positive ray photograph. It is necessary in experiments of this kind to reduce by a mercury pump the pressure to a fraction of a millimetre of mercury before applying the cooled charcoal.

We can, however, in experiments when the helium is liberated by prolonged bombardment eliminate this source of error, for if the helium and neon came from the air and not from the solid the amount of them produced would not depend on the length of the bombardment. I have checked in this way these experiments and have found that the helium is not appreciable unless the bombardment is prolonged for an hour or so and increases in amount with the length of the bombardment. Thus if the helium comes from the air the air must have been absorbed by the substance and the helium in it liberated by the bombardment.

To test whether this was the source of the helium I bombarded soluble salts such as LiCl, NaCl, KCl, KI, RbCl, $AgNo_{31}$ which were dissolved in water and also in some cases in alcohol and then evaporated to dryness, the process being in some cases repeated several times. Salts which had been treated in this way yielded helium and in some cases neon; the yield of helium from the salts of the alkali metals and in

particular from potassium was exceptionally large, KI giving a larger supply than any other of the substances I examined, with the exception of those like monazite sand which are known to contain large supplies of helium. Some of the salts have yielded apparently undiminished supplies of helium, after being dissolved and evaporated ten or twelve times. In order to see whether this process of solution and evaporation would get rid of dissolved helium, the following experiment was tried. It is well known that when the electric discharge passes through helium from aluminium electrodes, these electrodes absorb a considerable amount of helium. A piece of aluminium was divided into two portions, one half was made into electrodes of a vacuum tube filled with helium at the pressure of three or four millimetres of mercury and a current passed through the gas for two days, after this treatment the electrodes were dissolved in hydrochloric acid and evaporated to dryness. The salt thus obtained was then placed in the positive ray apparatus, bombarded by cathode rays for several hours, and a positive ray photograph of the gas given off was taken; it was found that the helium line was faint but perceptible. The other half of the aluminium which had not been near helium was then dissolved, evaporated, bombarded and the photograph taken, the intensity of the helium line in this case was but very little less than in the other, the difference not being greater than one would expect from accidental variations in the intensity of the discharge; this experiment shows, I think, that solution may be relied upon to eliminate absorbed gas.

The aluminum cathode in the tube used to bombard the substances with cathode rays might be suspected as a source of helium. If this were the case, however, the rate of production of helium would not depend upon the nature of the salt bombarded, nor would it make any difference as to whether the

cathode rays hit the salt or not. As both these conditions have a great influence on the rate of production of helium we may regard this source as eliminated. In addition to the preceding considerations some of the cathodes have been in almost continuous use for months without any perceptible diminution in the rate of supply of helium.

There is another possibility which it is much more difficult to eliminate by means of physical experiments, though the chemical properties of the inert gases may be thought to make it very improbable; this is that helium can combine with a large number of elements and that these helium compounds exist as impurities in the salts of these elements and that these compounds of helium, present as impurities in soluble salts, are also soluble. The fact that helium is given off by nearly every substance shows that this solid compound or compounds must be extremely widely spread if it is to explain the helium production. They must also possess very special chemical properties in order to explain a large number of cases of which the following is an example: if we take $AgNO_3$, a salt which will give some helium on bombardment, dissolve it in water, add HCl, we get a precipate of AgCl, now this silver chloride on bombardment will also give helium.

Thus if compounds of helium are present as impurities they must be precipitated by the same chemical reactions as precipitate the salts of the element with which they are mixed. It must I think be acknowledged that to explain the production of helium by the dissociation of helium compounds present as impurities obliges us to assign to helium chemical properties of a much more energetic kind than those usually assigned to it. On the other hand there are some effects connected with the appearance of helium which suggest that the source of this gas is not the whole mass of the salt but only a small fraction of it, and which would in fact be more

easily explained by the presence of an impurity than on the view that the cathode rays can detach helium from any atom, of potassium say, which they happened to bombard. One effect of this kind is the very considerable variation in the amount of helium which comes off from different specimens of the same salt when bombarded under apparently similar conditions, and sometimes also of considerable variations in different salts of the same metal; thus I have always got more helium from KI than from KCl. We must not, however, lay too great stress on this for it is difficult to ensure that the bombardment by the cathode rays is of the same intensity in any two experiments; a very slight variation of the pressure of the gas in the bombardment vessel might produce large variations in the energy of the rays striking against the salt.

Another effect, which also favours the impurity view, is that the rule of evolution of helium, unlike that of X_3 by the bombardment of potash, in nearly every case shows a tendency to diminish after long continued bombardment. This occurs even with salts which have been dissolved and evaporated to dryness. Experiments which are not yet completed are being made to see if the evolution of helium stops entirely after long continued bombardment. These effects could be explained and the difficulties attendant on the view that the helium comes from an impurity of the ordinary kind avoided by some such view as the following. The evolution of helium is not due solely to the bombardment, by the cathode rays. In the atoms of the ordinary elements and especially in those of the alkali metals a process is at work analogous to that which causes the expulsion of α particles from the atoms of the ordinary radio-active elements; the difference being that in the case of the ordinary elements the α particle, i.e. the helium, instead of being projected with the enormous velocity characteristic of radio-active substances, is projected

with so little energy that it does not wholly escape from the parent atom. It is loosened, so to speak, by effects which are analogous to radio-active effects and are independent of the cathode rays, the function of these rays is to detach the already loosened helium atoms. Thus it would only be certain atoms of the element which would yield helium when bombarded and when these were exhausted the supply of this gas would cease. The number of such atoms too might be expected to vary with different specimens of the same salt. Another view that might be suggested is that the helium might be formed in some such way as we have supposed X_3 to be formed, i.e. by the aggregation of atoms of hydrogen. If this were the case, however, we should expect that the formation of helium would be much more pronounced when the bombarded salts contained hydrogen than when they did not; as a matter of fact, however, some of the salts which yield the largest supply of helium such as KI do not contain any hydrogen.

The view that helium can be got from other chemical elements raises questions of such a fundamental character that few will be prepared to accept it until every other explanation has been shown to be untenable. It would greatly strengthen the proof if we could detect the parts of the atom which remain when the helium is spiit off. Experiments are being made with this object but there are very considerable difficulties to be overcome. The alkali metals have so far afforded the largest supply of helium; let us consider what the residues would be in this case. If we took He from Li the residue would probably be hydrogen, now hydrogen always occurs in the positive rays and no conclusion could be drawn from its occurrence when lithium was bombarded. Next take the case of sodium; the residue after the abstraction of helium would have the atomic weight $23 - 4 = 19,\frac{5}{3}$ which corresponds to fluorine, an element of such energetic chemical properties that it would probably

enter into chemical combination and escape detection; similar considerations apply to potassium, the residue from which might be chlorine—this again on account of its chemical properties would be difficult to detect. If we were to take elements of much greater atomic weight the residues would have high atomic weights also and these heavy atoms are not detected by the photographic plate nearly so easily as the lighter ones like helium, so that even if there were the same number of the atoms of the residue as of the helium present in the tube the helium might show on the plate while the residues did not.

The most promising elements for this purpose are light elements like carbon or beryllium whose residues would not coincide with any likely impurities in the tube. I have tried some experiments with pure carbon but hitherto have only been able to obtain such minute quantities of helium from it that it is impossible to draw any definite conclusions.

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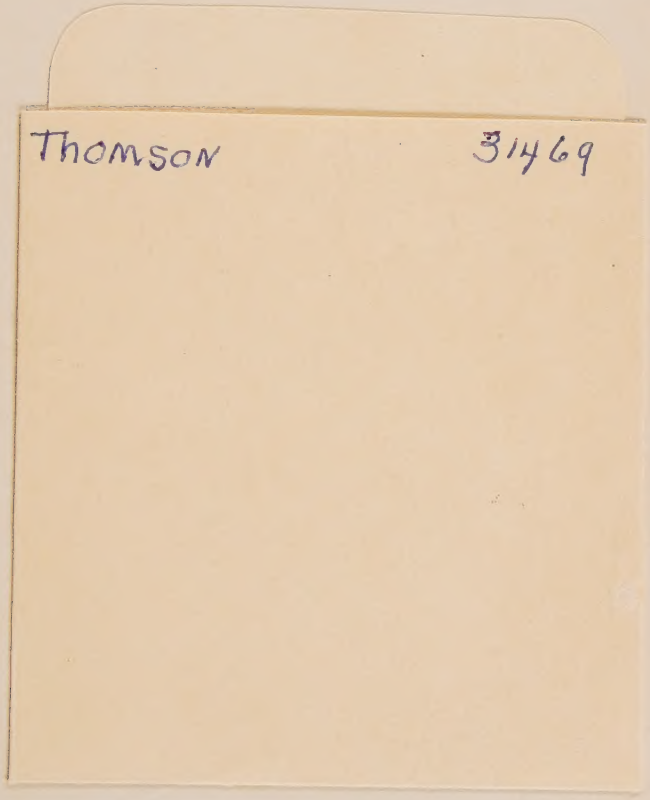
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